

Petroleum Hydrocarbons in Sediments from Jeddah Coast of Saudi Red Sea following the 1996 Fuel Oil Spill

SULTAN S. AL-LIHAIBI

*Marine Chemistry Department, Faculty of Marine Science,
Jeddah, Saudi Arabia*

ABSTRACT. The average concentration of extractable organic matter (EOM) in the sediments of the study area decreases in the order of Jeddah oil refinery > King Faisal Navy Base > Al-Salam lagoon/ Islamic Seaport. The concentration of petroleum hydrocarbons in the sediments being in the range of (0.9 to 281, mean 42.7 $\mu\text{g g}^{-1}$ dry wt) and (3.9 to 34, mean 12 $\mu\text{g g}^{-1}$ dry wt) for regions I and II respectively. The highest recorded value was found at the oil refinery zone.

The distribution of the aliphatic hydrocarbons of region I showed that the n-alkenes between C₁₄ and C₃₃ are present with great variability in the intensity. The input of recent oil was relatively substantiated by the presence of the n-alkenes (medium molecular weights). The contribution of the biogenic hydrocarbons (fatty acids) was also noticed in most of the samples analyzed. An Unresolved Complex Mixture (UCM) is present with great variability in the samples from same region. The oil residue of station 12 (oil refinery zone) was highly weathered, reflecting the absence of volatile components and most of the n-alkenes. The UCM signals of Jeddah oil refinery zone (*e.g.* station 12) was very high resulting from chronic oil pollution. The distribution of n-alkenes in the second region differs considerably from the first region of the study area probably due to influence of microbial degradation. The presence of the fatty acid in relatively high intensity compared with n-alkenes, indicates that the contribution from the natural source is significant in this region. Also, a homologues of alkenes in a relatively high quantity, in one of the extracts, is also reported from the second region only. Its presence in a series has not been observed previously. This ongoing project is to characterize and identify these compounds.

KEY WORDS: Extractable organic matter, Petroleum hydrocarbons, aliphatic hydrocarbons, Fatty acids, Sediments, Jeddah Coastal area, Red Sea.

Introduction

Oil pollution causes several damages to the marine environments and also to the economic impact. These damages depend on many factors *i.e.* type of crude oil, size of oil spill, location of the spill as well as the prevailing conditions (temperature, wind speed and sea state). Another factors change the fate of crude oil spilled into a marine environment and these including evaporation, water washing, photooxidation, biodegradation and the sediment nature (Vandermuelen and Singh, 1994). The composition of crude oil contains some components (aromatic compounds) that can be considered as toxic substances to marine organisms (Neff, 1979). However, their toxicity depends on the chemical structures of these compounds. Approximately 80% of the low molecular weight of the aromatic compounds can be lost from the water surface to the atmosphere through volatilization (McVeety and Hites, 1988).

The discharge of sewage wastewater and accidental shipping loss reached the marine environment with a considerable quantity of oil contamination. According to Kennish (1994), 45% of the oil pollution reaching the sea is derived from the land activity (*e.g.* river runoff, urban runoff, municipal wastes, ... etc.). While 33% of the oil pollution in the marine environment is related to oil transportation activities. Over the past decades there have been several oil spills from crude oil tankers and cargo ships on the Saudi Red Sea coast. For example, Kanchenjunga (1983) and Liverpool-Bay (1996) ships have spilled on the Jeddah coast. However, most of the oil spills have been occurred on the Saudi coasts were under control using the contingency plans by governmental organisations in Saudi Arabia *e.g.* MEPA, Saudi Aramco and Coast Guard. Moreover, the introduction of crude oil and its products into marine environments, through both operational and accidental releases, has been minimized due to governmental and public awareness.

Since the published literature concerning the petroleum hydrocarbons in marine environment of the Saudi Red Sea coast is very limited, this study therefore was intended to contribute more information regarding the level of oil pollution and also the distribution of aliphatic hydrocarbons in the vicinity of Jeddah coast after spill of fuel oil (bunker C) from cargo ship "Liverpool-Bay".

Materials and Methods

Study Area

The study area is located in central of Saudi Red Sea coast (Fig. 1). This area is characterized by the presence of Jeddah oil refinery, Al-Arbaeen, Al-Shabab and Al-Salam lagoons as well as the Seaport. The study area can be classified into two regions according to the source of organic pollution. The source of oil

pollution in region I comes from the oil refinery and the activities related to oil transportation (*e.g.* normal operation losses, accidental spill ... etc.). Recently, the region was affected by the spill of fuel oil (bunker C) from cargo ship “Liverpool-Bay”. The accident was reported on March 1996. It was estimated that more than 200 tons of bunker C fuel oil were spilled. The countermeasure of such type of oil spill in a marine environment can be summarized as follows: (i) little or no evaporation, (ii) heavy contamination of intertidal area, (iii) long-term contamination of sediments, (iv) weathering processes are very slow and (v) shoreline clean up is difficult under all conditions. However, the clean-up of the spilled fuel was conducted right away after the accident under the supervision of Meteorology and Environmental Protection Administration (MEPA) and Saudi Aramco. After 6 months the region was visited and surveyed by our group. It has been found that the residue of the spilled fuel oil is still present in some locations. The tar mats were found along the coast and in the intertidal area. In addition, the presence of Jeddah oil refinery is considered as a permanent oil contamination source in the region. The sampling of sediments from this region was undertaken 18 months after the spill (September 1997) and all the samples were collected from a depth below 10 m.

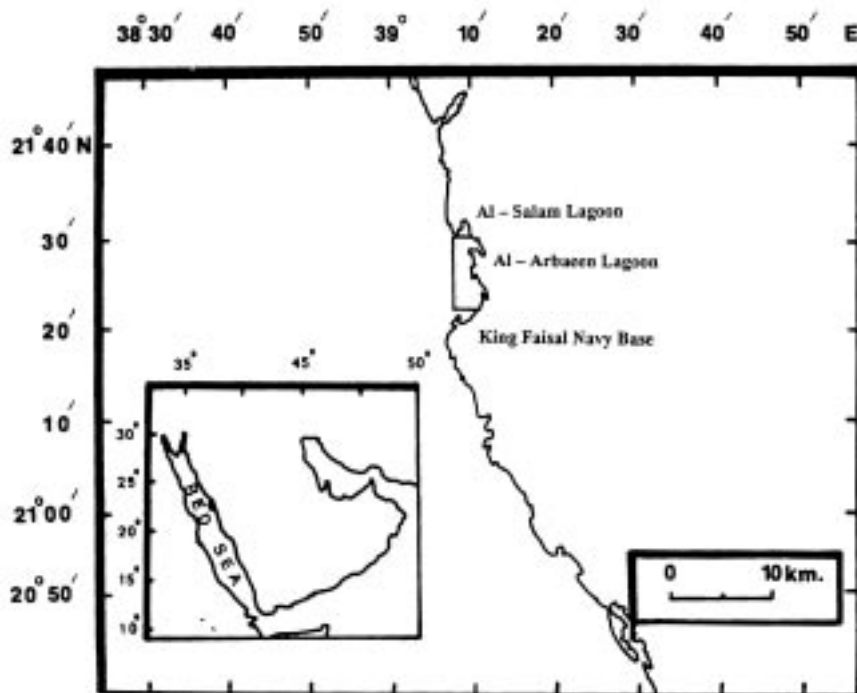


FIG. 1. Map of study area from the coast of Saudi Red Sea.

The second region is surrounded with three lagoons and oil pollution was mainly derived from the discharge of the municipality waste. The three lagoons are heavily contaminated as a result of the discharge of partially treated sewage wastewater. For example, 40,000 m³ d⁻¹ discharge daily into Al-Salam lagoon and relatively similar quantity also discharge into Al-Shabab lagoon (personal communication). The sampling of the sediment from the region between the entrance of Al-Salam lagoon and Islamic seaport and the sampling time was during the month of June, 1997.

The collected samples were frozen at -20°C and then were homogenized and freeze-dried. The freeze-dried sediments were stored in pre-cleaned amber glass bottles until analysis.

Extraction and Analysis

Petroleum hydrocarbons

The dried sediments (*ca.* 7 g) were extracted with a mixture of dichloromethane and methanol (1:1 v/v), using soxhlet apparatus for 24 hr. After the extraction, the solvent was removed by rotary evaporator and the extracts were completely dried under clean nitrogen. The extractable organic matter (EOM) of the sediment samples was gravimetrically measured using microelectrobalance. The method of estimation of petroleum hydrocarbons residue was followed by the IOC/UNESCO (1991) using UVF technique. Light Arabian crude oil was used as standard for quantification and the estimation of the PAHs in sediments was read at excitation 310 nm/emission 360 nm.

Aliphatic petroleum hydrocarbons

The sediment extracts of selected samples from the study area were fractionated by column chromatography on 8 g of silica. The saturated fraction was eluted with 30 ml hexane. The extracts were concentrated to approximately 3 ml using a rotary evaporator, and the remaining solvent was then dried under a gentle stream of nitrogen gas. Elemental sulphur was removed from the extracts using activated copper.

Gas chromatography mass spectrometry (GCMS) analyses of the aliphatic fractions were made on a Shimadzu GC-17A gas chromatograph equipped with split/splitless injector, and a DB fused silica column (25 m × 0.3 mm i.d., 0.17 µm DB-1% phenyl/99% methyl-silicon) using helium carrier gas. The GC conditions were as follows: the temperature programming (40-300°C at 5°C/min then isothermal for 5 min); the injection port temperature was 250°C and helium was as carrier gas (flow rate *ca.* 2 ml min⁻¹). The end of the GC column was introduced into the electron impact (EI) source of a Shimadzu QP-5000 Quadru-

pole mass spectrometer. Typical mass spectrometer operating conditions were as follows: transfer line 230°C, ion source 250°C, electron energy 70 eV. All samples were analyzed in full data acquisition (SCAN) mode by scanning from 50-500 daltons at 1 cycle/s. Identification of the compounds was based on comparison of retention indices and mass spectra.

Results and Discussion

Extractable Organic Matter

The EOM contents in the sediments from region I ranged from 7.3 to 26.4 mg g⁻¹ (Table 1 & 2). The highest recorded value of EOM was observed at station 14 which is very close to oil refinery. The data in this region has been classified into two sub-groups according to the average of total concentrations of EOM. Thus, the average concentrations of EOM in sediments from Jeddah oil refinery zone (stations 11, 12, 13 and 14) was 21.2 mg g⁻¹. Whereas, in stations 1-10, the value was 11.7 mg g⁻¹. In the second region, the concentration of the EOM in sediments varied from 3.4 to 20.3 mg g⁻¹ (Table 2). The average concentration of EOM in the sediments of Jeddah oil refinery was higher by 1.7 times than the average of the second region. In contrast with values of EOM recorded by Fowler *et al.* (1993) and Al-Lihaibi and Ghazi, 1997 for the Arabian Gulf sediments, the present results showed much higher levels for the Red Sea sediments. The differences in the EOM contents in this study with that of Fowler *et al.* (1993) may be related to the method of extraction. In the present study, the extraction with dichloromethane: methanol solvent ensures most of the extractable material dissolution and consequently higher EOM concentration than that expected from the n-hexane solvent extraction used by Fowler *et al.* (1993).

Petroleum Hydrocarbons

Concentration of petroleum hydrocarbons in sediments from the study area is presented in Tables 1 and 2. The petroleum hydrocarbon contents in the sediments from region I vary from 0.9 to 281 µg g⁻¹ dry weight. Jeddah oil refinery zone (stations 11, 12, 13 and 14) exhibited the highest concentrations of petroleum hydrocarbons among the other stations of the region. The second region showed values ranging from 3.9 to 34 µg g⁻¹ dry weight (Table 2). The average of the total concentrations of Jeddah oil refinery zone (104 µg g⁻¹ dry weight) exceed eight times the averages of stations 1-10 from the same region (13.8 µg g⁻¹ dry weight), as well as the second region (12.3 µg g⁻¹ dry weight). Awad (1985) reported that the level of oil residue in the effluents waters from the oil refinery was very high. Thus, the relatively elevated oil residue in the oil refinery zone is attributed to the discharge of the oil refinery effluents as well as the maritime transportation activities.

TABLE 1. Concentrations of extractable organic matter (EOM) and total petroleum hydrocarbons (TPHs) in sediments from region I off Jeddah coast, Saudi Red Sea.

Station no.	EOM mg g ⁻¹	TPHs µg g ⁻¹
1	7.4	1.7
2	10.63	0.9
3	11.9	n.d.
4	11.7	7.6
5	21.4	69.4
6	9.7	3.8
7	10.4	6.7
8	9.6	8.8
9	7.3	3.9
10	16.6	35.2
11	17.5	42.9
12	25.1	281.5
13	15.7	51.9
14	26.4	40.7
average	14.4	42.7

n.d. = not determined.

TABLE 2. Concentrations of extractable organic matter (EOM) and total petroleum hydrocarbons (TPHs) in sediments from region II off Jeddah coast, Saudi Red Sea.

Station no.	EOM mg g ⁻¹	TPHs µg g ⁻¹
1	4.5	6.4
2	5.2	9.3
3	6.9	34.0
4	n.d.	n.d.
5	21.4	69.4
6	3.4	10.2
7	8.2	8.0
8	17.7	9.9
9	6.5	3.9
10	16.6	35.2
11	5.6	3.9
12	20.3	5.0
13	6.8	24.8
14	11.1	12.8
15	5.8	17.8
16	8.2	9.8
17	12.9	33
18	6.2	8.4
19	12	8.7
average	8.6	12.3

n.d. = not determined.

It is noteworthy that 42% of the data set from region I represents relatively high level of petroleum hydrocarbons ($> 30\mu\text{g g}^{-1}$), while this level represents only 5% of data from the second region. Also, it is worth indicating that on the basis of the total petroleum hydrocarbons, the sediments from the studied area are consistent with many subtidal sediments reported from various large spill areas (Lee and Page, 1997).

Aliphatic Hydrocarbons

The distribution of the aliphatic hydrocarbons in the sediments of the selected samples from the study area was investigated. Figures 2, 3 and 4 show the distribution of aliphatic hydrocarbons in distinct sample extracts. The total ion chromatographic patterns of these samples were quite variable. It has been found that the n-alkenes with chain-lengths ranging C_{14} - C_{33} were present in most of the sample extracts and the medium molecular weight (C_{18} - C_{26}) were relatively the most abundant (*e.g.* station 5) in region I. The abundance of these range of n-alkenes over the whole distribution may suggest a recent oil input (Readman *et al.*, 1986). The plausible explanation for such input of oil into the sediments of this region (subtidal area) is probably due to erosion of oiled sand from the deposited oil on the beaches and also from batches of the tar balls and/or tar mats deposited on intertidal area. Hayes *et al.* (1993) have reported that half of the oil originally deposited on the beaches of the Saudi Arabian Gulf after 1991 oil spill were eroded and transported into the nearshore sediments.

The presence of the two isoprenoid alkenes pristane (pr) and phytane (ph) was detected in the extracts with very low abundance. The origin of the pristane is possibly derived from algae and bacteria (Blumer *et al.*, 1971), while phytane is originated from both biogenic and abiogenic sources. However, these components are common in sediments and most crude oils. In addition, several compounds (fatty acids) with relatively high abundance were recorded in aliphatic chromatograms of some extracts (*e.g.* stations A9 and 18). The origin of these compounds could be related to a biogenic source. It is worth indicating that the presence of the EOM in a relatively high levels in the sediments, reveal the association of the biogenic as well as the abiogenic materials.

The UCM also showed a great variability in the extracts of the samples. The composition of the UCM consists of a branched and cyclic compounds and they are resistant to weathering and biodegradation processes. It has been found that the UCM in most of the extracts was extended over a wide range. Sample from Jeddah oil refinery zone (station 12) showed that the low volatile components and nearly all n-alkenes were depleted as consequences of high weathering. Also, the presence of the high UCM signal in this station among the other stations indicated that the sample was exposed to the most chronic oil pollution. However, the presence of UCM has frequently been interpreted as strong evidence of oil contamination (Farrington *et al.*, 1977).

In the second region (II) of the study area, the distribution of the aliphatic hydrocarbons in the selected extracts of the sediment samples differs, to large extent, from those reported in region I (Fig. 4). The distribution shows that the n-alkenes are present in a relatively low intensity. The presence of these n-alkenes with low intensity indicates that the microbial degradation of these compounds is

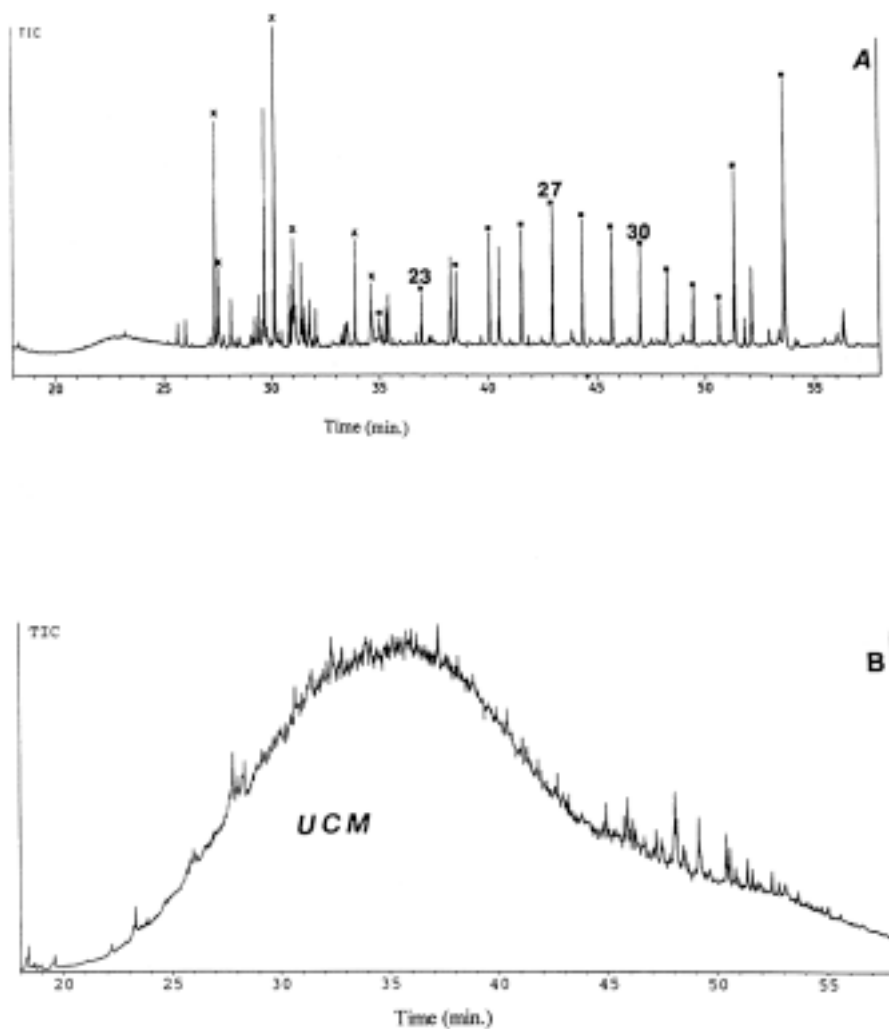


FIG. 2. Total ion current (TIC) chromatograms of aliphatic hydrocarbons isolated from the sediment from region I. A = sample collected from the barrels during cleanup operation (mixture); B = (station 12); UCM = unresolved complex mixture; x = Fatty acids. = n-alkanes and number refer to carbon number.

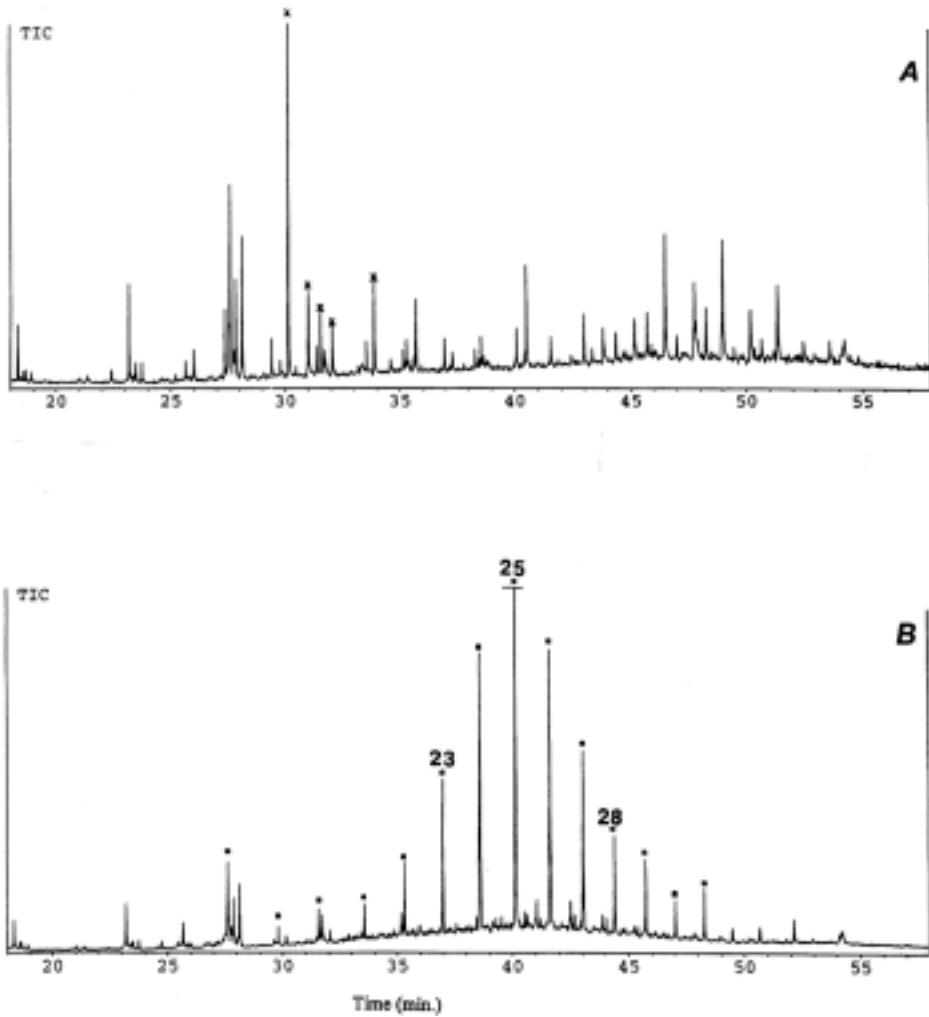


FIG. 3. Total ion current (TIC) chromatograms of aliphatic hydrocarbons isolated from the sediment from region I. A = (station 9), B = (station 5); x = Fatty acids. = n-alkanes and number refer to carbon number.

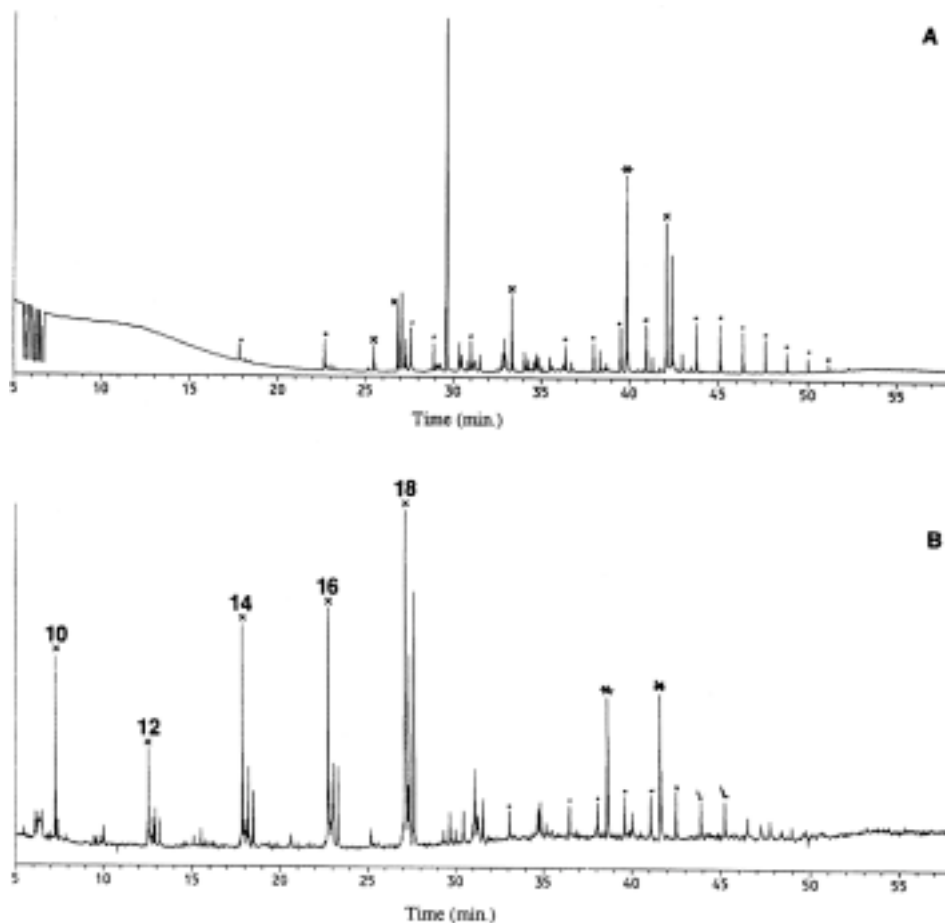


FIG. 4. Total ion chromatograms (TIC) of aliphatic hydrocarbons isolated from the sediment from region II. A = (station 18), B = (station 19); x = Fatty acids. * = unknown, + = n-alkanes, . = n-alkanes and number refer to carbon number.

probably the forcing factor in this region. The other type of the aliphatic hydrocarbons (isoprenoid alkenes) as well as the unresolved hydrocarbons (UCM) were not detected. While, the fatty acids were found in a relatively high intensity in most of the extracts being in the range of C_{15} - C_{23} , the presence of these compounds is generally indicative of biogenic autochthonous inputs (phytoplankton, zooplankton and algae). Several studies have reported the same fatty acids composition in marine sediments (*e.g.* Volkman *et al.*, 1983; Mille *et al.*, 1992).

It is worth indicating that homologues of n-alkenes were detected in samples of station 19 from the second region. The n-alkenes with chain lengths ranging from 12 to 18 carbon atoms were relatively predominant in the sediments from station 19. Figure 5A shows the distribution of the homologous of n-alkenes with their isomers, while Fig. 5B shows the spectrum of the major C_{18} -alkenes. The isomers of these alkenes were not identified. These homologues were not observed in the other region of the study area. The preliminary hypothesis for their original may come from the microbial decomposition of large molecules. However, the presence of alkenes (normal, branched and cyclic) have previously reported in marine sediments in trace amount. For example, Mille *et al.* (1992) has found two n-alkenes compounds (C_{16} and C_{17}) in sediments with smaller quantity. To my knowledge, the presence of these n-alkenes in a relatively large quantity with this distribution from Saudi Red Sea coastal area in particular has been reported for the first time. It is worth noting that the investigation of these compounds is ongoing project and it will be published very soon.

Conclusions

The total petroleum hydrocarbons associated with sediments are within the range published in the literature for subtidal areas. The discharge of the effluents from the oil refinery zone exhibited an elevated concentration of petroleum hydrocarbons in sediments among the other zones of the study area.

The distribution of aliphatic hydrocarbon revealed that the study area is having a hydrocarbon contribution from biogenic and abiogenic sources. The input of recent oil pollution into region I comes from the erosion of the oiled sands deposited on the beaches and intertidal after the spill. While, the discharge of oil products as a result of the wastewater discharge and road runoffs in the second region has been observed, the high signal of the UCM in the oil refinery zone explains that the zone exposes to the most chronic oil pollution. Also, the composition of the aliphatic fraction (low molecular weights and most alkenes) in station 12 was missing as a results of high weathering. The distribution of fatty acids in most sediments is indicative of biogenic autochthonous inputs. The presence of a homologues of n-alkenes in the sediments from the second region is for the first time reported, however the origin of these n-alkenes is not clearly obvious.

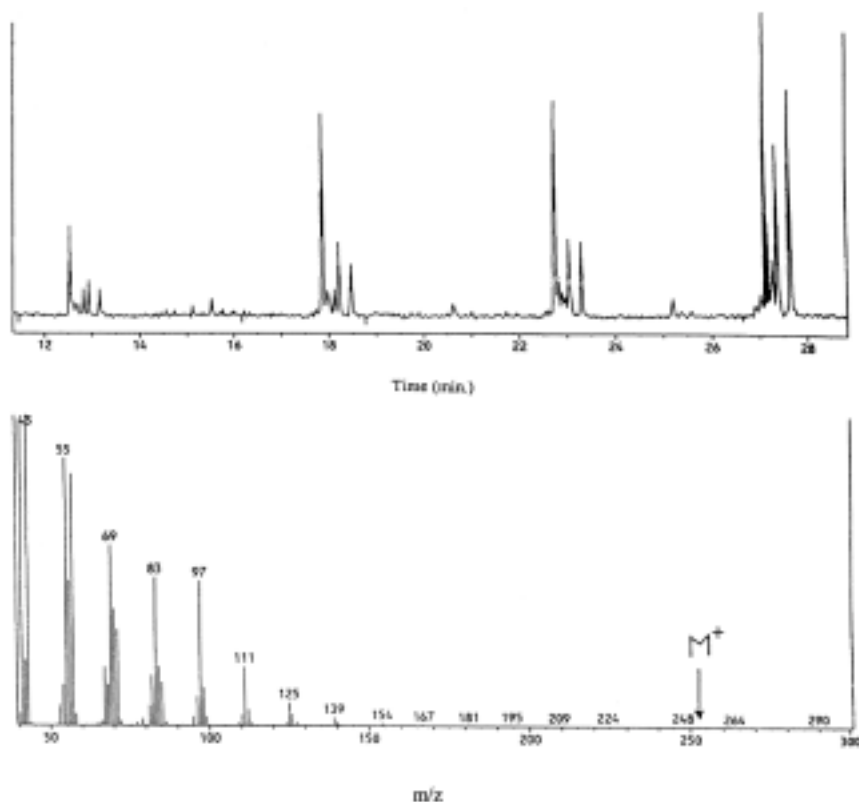


Fig. 5. Partial total ion current of aliphatic hydrocarbons of sediment extract from sediments from region II (A) station 19 and (B) Mass spectrum (background corrected) of the C18-alkane present in sediments from above station.

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الهيدروكربونات البترولية في رسوبيات ساحل البحر السعودي (مدينة جدة) بعد حادثة تسرب زيت الوقود في عام ١٩٩٦م

سلطان س . الهبيبي

قسم الكيمياء البحرية ، كلية علوم البحار ، جامعة الملك عبد العزيز

جدة - المملكة العربية السعودية

المستخلص . أظهر معدل تركيز المواد العضوية المستخلصة بالمذيبات العضوية في رسوبيات منطقة الدراسة تناقصاً بدءاً من مصفاة جدة إلى قاعدة الملك فيصل البحرية (منطقة رقم I) إلى المنطقة المحصورة ما بين بحيرة السلام وميناء جدة الإسلامي (منطقة رقم II) ، بينما وجد أن تركيز الهيدروكربونات البترولية في الرسوبيات يتراوح ما بين ٩, ٠-٢٨١ مايكروجرام / جم وزن جاف في منطقة رقم I ، و ٩, ٣-٣٤ مايكروجرام / جم وزن جاف في منطقة رقم II كما لوحظ أن أعلي تركيز للهيدروكربونات البترولية يوجد في عينات مصفاة جدة .

وبدراسة توزيع المركبات الأليفاتية في منطقة I وجد أن الألكانات توجد ما بين كربون ١٤ - كربون ٣٣ مع الاختلاف في الكمية . كما لوحظ وجود الألكانات ذات الأوزان الجزيئية المتوسطة في وضع مسيطر مما يعطي دلالة على أن المنطقة تتعرض لإضافة مواد بترولية حديثة ، قد تكون من تلك الموجودة على الساحل . بالإضافة إلى ذلك لوحظ وجود مركبات ذات أصل بيولوجي طبيعي (الأحماض الدهنية) . كما يمكن القول أن عينات منطقة مصفاة جدة تعطي دلالة واضحة على أن التلوث بالزيت في تلك المنطقة يصنف على أنه تلوث مزمن .

أما بالنسبة لتوزيع الألكانات في رسوبيات منطقة رقم II فهي نسبياً توجد بكمية أقل مقارنة مع منطقة رقم I وقد يعود السبب إلى تأثير الكائنات الدقيقة التي تقوم بدور التكسير لهذا النوع من الهيدروكربونات بسهولة . كما لوحظ وجود كمية من الألكينات في عينة واحدة من رسوبيات منطقة رقم II ، حيث تراوح عدد ذرات الكربون لتلك الألكينات من كربون ١٢ - كربون ١٨ . هذا التوزيع لم يلاحظ في عينات رسوبيات المنطقة الأخرى فضلاً على أن الدراسات السابقة لم تشير إلى مثل هذا التوزيع من قبل .