Monitoring and Assessment of Petroleum Hydrocarbons in Surface Seawater along Alexandria Coasts, Egypt

[1]**Omayma E. Ahmed** , [1]**Sawsan A. Mahmoud and** [2]**Abd El Rahman M. Mousa**

[1] *Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt*
[2]*Ain Shams University, Cairo, Egypt*

ABSTRACT

A study on petroleum hydrocarbon concentrations in seawater along the coast of the Alexandria, Egypt was conducted during 2014 - 2015. The concentrations of dissolved/dispersed petroleum hydrocarbons (DDPH) in seawater samples were measured at 13 stations, analyzed by gas chromatography; Ultraviolet and FT-IR spectrometry techniques to determine the probable type and/or source of any petroleum pollutants present. The concentrations were found to be in the range 2421 and 183817 µg/L, with a mean value of 25613.885 µg/L. An attempt was made to compare between petroleum hydrocarbons in Alexandria seawater with many other marine coasts, total petroleum hydrocarbons in surface sea water are found to be above the admissible environmental levels. Different diagnostic criteria such as unresolved / resolved compound ratio, pristane / phytane, carbon preference index of *n*-alkanes, pristane / *n*. heptadecane and phytane / *n*. octadecane were used to distinguish between petrogenic and biogenic inputs. Results of the present study have led to better understanding of factors controlling the processes of pollution of in Alexandria sea waters and provide important implications when implementing mitigation pollution management planes for the Alexandria Harbors. In view of mitigation, the outfalls from shipment activities loading / unloading operations and municipal agricultural waters resulting from Alexandria Governorate should be controlled for the benefit of the public health and the aquatic life.

Key words: Dissolved / dispersed petroleum hydrocarbons, Petrogenic, Biogenic, Oil contamination, Alexandria Coastal area

Introduction

The coasts of the Mediterranean specially city of Alexandria is a major tourist attraction for their clear waters and coastal habitats, and is vital for fisheries and marine activities. However, the coasts are under constant threat of petroleum pollution in the form of untreated domestic sewage, oil transportation, oil spillage and ballast water from tankers, and industrial waste waters. Furthermore, the western region is subjected to petroleum contamination from different sources such as the western desert oil fields and the Suez-Mediterranean pipeline terminal (SUMED) 27 km west of Alexandria. Efficient and unambiguous analytical methods for the characterization of these spillages are needed in order to (1) determine defensibly the source of the oil, (2) distinguish spilled oil from background hydrocarbons (3) evaluate the extent of impacted ecosystems in a quantitative manner, and (4) enforce the pollution control laws. The methods using biomarker and hydrocarbon components offer the distinct advantages of being able to withstand interference from heavy weathering effects and to identify and match the spilled oil source, (Sharkawi, 1985) studied pollution of the beaches of Alexandria due to discharges of sewage. A part of the city sewage is discharged into the sea through some outfalls along the coast, which is suggested to be the reason of some epidemic diseases. The eastern harbor in Alexandria is presently polluted by discharge of wastewater effluents from different sources. It has recently been decided to restore this important coastal area by (1) stopping the direct discharge of wastewater effluents into this semi-enclosed harbor in 1993 and (2) gradually reducing the discharge of the municipal wastewater through marine outfalls at two sites lying at the outer sides of the harbor. To protect many invaluable under water buildings of archaeological interest in Alexandria at different sites in the eastern harbor of Alexandria, it is important to improve the water quality of an open sea, and comparative studies were done on water quality in the harbor after 1993, 1996, 1999-2000. The results reveal that the harbor is expected to become meso/oligotrophic as soon as the complete cessation of the discharge from the two outside sources is attained, (Osman, *et al.,* 2003). In this study, GC techniques are used to identify the type and to assess the source of representative aliphatic hydrocarbons samples collected from several locations along the coast of Alexandria; the assessment relies upon analyzing individual aliphatic. High concentrations of hydrocarbons have been recovered in the Alexandria coasts compared to the surface water in various coastal environments (Guitart, *et al.,* 2007). Aliphatic

Corresponding Author: Omayma E. Ahmed, Department of evaluation and analysis Egyptian petroleum Research institute
Nasr City, Cairo, Egypt
E-mail: dr.omaymamosa@yahoo.com

hydrocarbons (AH), which may be of biogenic or anthropogenic origin, consist of a series of resolved compounds (R) and of unresolved complex mixture (UCM) hump. Concerning the distribution of the resolved compounds, an elevated proportion of C_{15}–C_{23} *n*-alkanes indicate that unburned lubricating oils from road traffic exhaust are a significant contributor to aliphatic hydrocarbons (Simoneit, 1985). Furthermore, the carbon preference index (CPI) in the range nC_{21}–nC_{33}, computed from the ratio of odd to even numbered *n*-alkenes, provides useful information about the AH origin. Indeed, high values of CPI_{21-33} are characteristic of terrestrial higher plant debris. For instance, epicuticular waxes of higher plants typically have *n*-alkane maxima at C_{27}, C_{29} and C_{31} (Rielley, *et al.,* 1991). On the contrary, lower CPI_{21-33} values are consistent with chronic petroleum inputs (Wang, *et al.,* 1997). Pristane (Pr) to phytane (Ph) ratio is also of interest since high values are reliable indicator of the absence of petroleum and clearly indicate a marine biological origin (UNEP/IOC/IAEA, 1992) although low values do not reflect the presence of petroleum (Humphrey, *et al.,* 1987). As for the unresolved compounds, the UCM hump is generally considered as to be a mixture of many structurally complex isomers and homologues of branched and cyclic hydrocarbons that cannot be resolved by capillary gas chromatography (GC) columns (Bouloubassi, *et al.,* 1993). The presence of UCM is the sign of a petroleum input and / or the presence of biodegraded complex mixture of hydrocarbons. Its relative importance, expressed as the ratio of unresolved to resolve compounds (UCM/R), is commonly used as diagnostic criteria of pollutant inputs (Mazurek, *et al.,* 1984). The threshold value of UCM/R that confirms the widespread presence of petroleum-related residue is 4 according to (Lipatou, *et al.,* 1991). This contamination has harmful consequences on the natural resources. The objectives of the present study are to characterize background hydrocarbon concentrations (HC) in surface water between EL-Montazah beach and Sidi Krier beach; located 42 km along the coast; to determine predominant origins, biogenic and petrogenic sources of hydrocarbons using molecular indices in the hydrocarbon; to assess the evolution of HC assemblages between the industrialized and the rather pristine areas along the coast and to compare the level of hydrocarbons contamination along the Alexandria coast with other Mediterranean sites.

Methods and Materials

Area of study

The investigated area lies between longitudes 29° 30` W, 30° 30` E and latitudes 31° 00` S to 31° 30` N. Figure 1. This shows also the location of sampling stations. It comprises most of the coastal area of Alexandria, extending from EL-Montazah beach at the northeast to Sidi Krier beach at the northwest with a shoreline of about 42 kilometers long. The area includes three harbors; the two old harbors (the Western and Eastern Harbors) and the newly constructed El- Aldekhela harbor. The northeastern part of the area comprises most of the old beaches EL-Montazah beach, Miami beach, 26-July beach beside, the east port of Alexandria while, the west port of Alexandria, EL-Nikhil Beach, EL-Bitash Beach, EL-Hanovill Beach, 6-October Beach, Center the drainage a Gamy (km.21) and Sidi Krier beach at the northwest. The coastal sea area of Alexandria, which comprises the biggest and main harbors in the country and is considered one of the most industrialized zones, receives considerable amounts of petroleum and its products.

Collection of wastewater samples

The samples are collected from the different sites in the studied area as described in Table 1 & Figure 1. The surface wastewater samples *(0-2cm)* were taken along the coasts of Alexandria sea using plastic water sampler for wastewater analysis, the sample size was (3L.) for analysis and cleaned before use; they were rinsed several time in (0.1N) HCl for several days and then rinsed and protected in diluted acid to prevent degradation of oil to give proper result of analysis. During the period of study, the wastewater samples are collected from two sides of the location and mixed to make composite sample which represent one station.

Extraction of petroleum oil from seawater samples

100 ml of the surface seawater sample was shaken with 100 ml of carbon tetrachloride in a separating funnel for 15 minutes. After 30 seconds agitation and 3 minutes settling period, the aqueous layer was discarded. The process was repeated until all of seawater sample has been extracted. The obtained extract was dried using anhydrous sodium sulphate (30g). The extract was then transferred to a weighted beaker and finally evaporated by electrical furnace at 60 ^{0}C till constant weight (Nazik, *et al.,* 2013).

The oil content was calculated as: μg of oil/L $= \dfrac{(A-B) \times 10^{(6)}}{mL\ of\ water\ sample}$

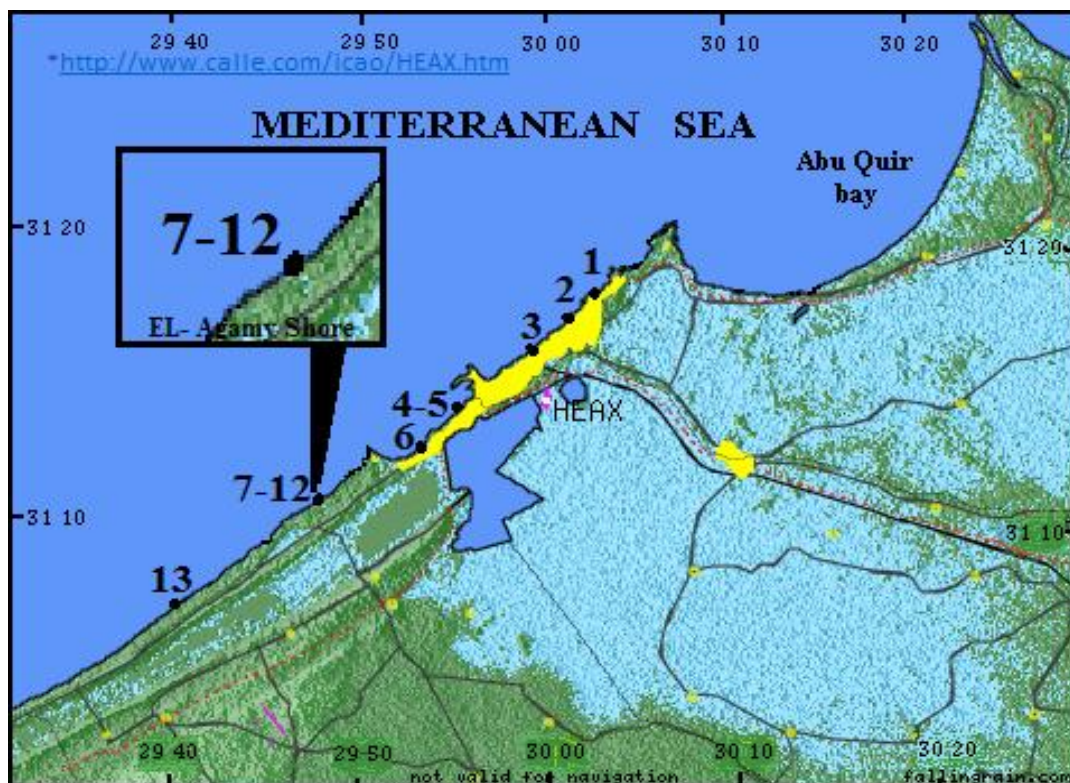Where: A & B are the weight of flask after and before extraction.

Fig. 1: Map of study area, showing sample points from Alexandria coastal seawaters, Egypt.

Table 1: Studied sites, their locations, activities and distance from EL-Montazah beach

Site No.	Location	Activities	Distance from EL-Montazah beach (km)
1	EL-Montazah Beach	Recreational	0.0
2	Miami Beach	Recreational	2
3	26-July Beach	Recreational	8
4	The east port of Alexandria	Loading and un-loading of ships, Producing	10
5	The west port of Alexandria	lubricants oil and sewage wastes,	11
6	The west port of Aldekhela	Chemical industries.	13
7	EL-Nikhil Beach	Recreational	35
8	EL-Bitash Beach	Recreational	36
9	EL-Hanovill Beach	Recreational	37
10	Zahra El-A Gamy	Recreational	38
11	6-October Beach	Recreational	39
12	Center the drainage a Gamy (km.21)	Recreational and agricultural drainage	40
13	Sidi Krier Beach	Summed pipelines and power station	42

Km: kilometers.

Gas chromatography analysis

All the oils-extracted from the studied water samples were analyzed using capillary column according to the standard test method IP318/75 (IP Standard 1993; Omayma, *et al.,* 2014) for Analysis and Testing of Petroleum and Related Products. Agilent Technologies 7890 A, Gas Chromatograph System, FID with HP-5, 30 m Length, 0.320 mn film thickness capillary Column. The Carrier gas was helium at flow rate of 2 ml / min. The injection volume was 0.1 µI. Oven temperature increased from 80℃ with a rate of 3℃/min up to 300 ℃. The injector temperature and detector temperature were 320 ℃.

Results and Discussions

Hydrocarbon analysis of Alexandria Coastal waters

Dissolved/dispersed petroleum hydrocarbon (DDPH) concentration in seawater samples

Analysis of the seawater samples taken from 13 stations in the north of Alexandria Sea yields the total of DDPH concentration values as shown in Table 1 and Figure 2. The obtained DDPH concentrations are within the range of 2421 and 183817 µg/L with a mean value of 25613.885 µg/L, DDPH concentrations in seawater can be grouped into two general areas, namely the harbors and coastal beaches along the northeast and northwest parts of Alexandria coastal sea water. The DDPH concentrations of the harbors stations were in the range between 4090-2350.9 µg/L, with the mean value of 4038.067 µg/L, the west port of Alexandria 2350.9 µg/L seemed to be less polluted than the east port of Alexandria (5673.3 µg/L), beside west port of Aldekhela 4090 µg/L was less than two Western and Eastern ports of Alexandria, this is consistent with the prevailing surface water current (direction from northwest to east). While, the coastal beach concentrations were found in the range of 2421 - 183817 µg/L with an average value 318476.8 µg/L however the data indicated significant difference between the mean of the harbors stations as compared to coastal beaches area. This is due to the harbors are severely affected by marine transportation activities tankers, cargoes ships (Finn, *et al.,* 1979). Although the harbors is provided by oil basin situated under the openings connected to oil leakage during unloading the crude oils yet, human errors, neglicancy and harbor traffic contribute effectively to the petrogenic pollution while, the coastal sea beach receives hydrocarbons from the sea are often found due to the effluents of sewage outfalls, industrial discharge, ballasting and de-ballasting operations of oil tankers and atmospheric rain-out which includes incompletely combusted oil products which reflect the influences of anthropogenic activities. Figures 4&5 shows elevated concentrations of DDPH in water samples of Zahra El-A Gamy near 6-October beach, particularly at station 10 which has the highest DDPH concentration of 183817 µg/L, this is related to the releasing of petroleum wastes from passing ships while parking at the waiting zone nearby the harbors and fuel catering processes, the presence of a cavity next to the beach in the works on assembling the accumulation of petroleum contaminants. However, the high DDPH concentrations at station 7 and 8 would be probably due to the effluents of sewage outfalls, industrial discharge, ballasting and de-ballasting operations of oil tankers. Moreover, the high value at center of the drainage a Gamy (km.21) 41903 µg/L, as a result of pouring all types of agricultural, industrial, and animal effluents directly to the sea. It is generally stated that water could be considered polluted when the hydrocarbon concentration is higher than 2.0 ug/L (Keizer, *et al.*, 1973), generally the concentration of oil in beaches found in increasing order, were 26-July Beach (2421 µg/L) < Sidi Krier Beach (2655 µg/L) < EL-Montazah Beach (5068 µg/L) < Miami Beach (5172.3 µg/L) < EL-Hanovill Beach (8933 µg/L) < EL-Nikhil Beach (26079 µg/L) < EL-Bitash Beach (38182 µg/L). This is attracts a huge public concern as the on-going recreational activities on beaches get seriously affected, which in turn affects the tourism industry, and the Government of Egypt is concerned about this environmental problem. In view of mitigation, the outfalls from shipment activities loading / unloading operations and municipal agricultural waters resulting from Alexandria Governorate should be controlled for the benefit of the public health and the aquatic life.

Table 2: Oil content (µg / L) extracted from Alexandria coastal waters

S.NO.	Location	Oil content (µg/L)
1	EL-Montazah Beach	5068
2	Miami Beach	5172.3
3	26-July Beach	2421
4	The east port of Alexandria	5673.3
5	The west port of Alexandria	2350.9
6	west port of Aldekhela	4090
7	EL-Nikhil Beach	26079
8	EL-Bitash Beach	38182
9	EL-Hanovill Beach	8933
10	Zahra El-A Gamy	183817
11	6-October Beach	6636
12	Center the drainage A Gamy (km.21)	41903
13	Sidi Krier Beach	2655

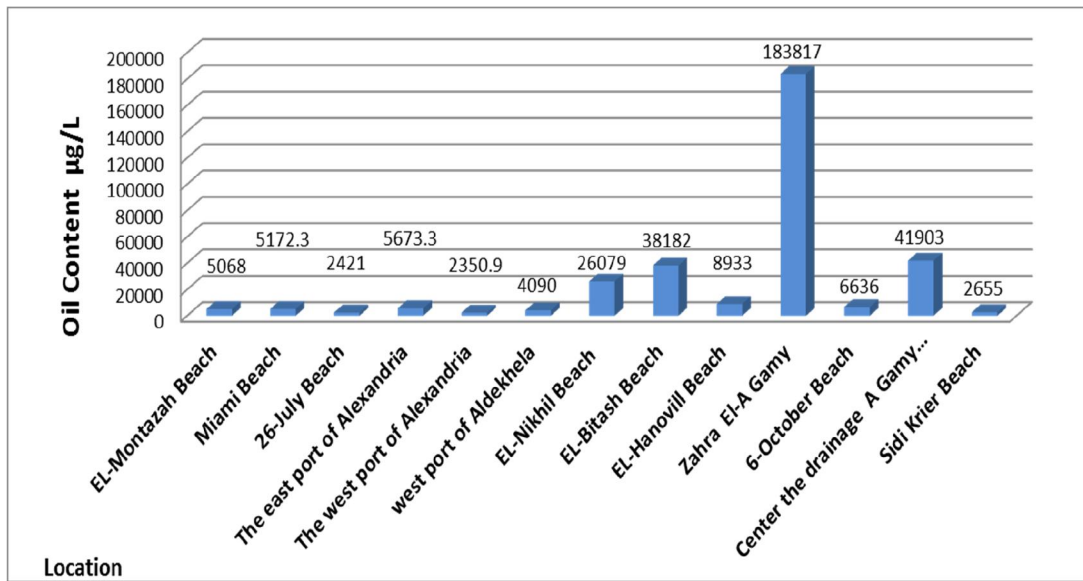**Fig. 2**: Histogram represented oil content (µg/ L) extracted from Alexandria coastal seawaters

Risk assessment of Dissolved/dispersed petroleum hydrocarbon (DDPH) concentration in Alexandria coastal waters

The hydrocarbons contamination in Alexandria coastal area were much higher than the limit No. 4 /1994 (50 µg /L) permitted by Egyptian law of Environment, which is a directive concerning the quality of sea water intended for human consumption (Shereet, 2009). Petroleum concentrations as low as *1–10 µg/L* can cause chronic disruption of sensitive organisms (e.g., behavioral activities of aquatic larvae such as feeding and reproduction). The State of Alaska Department of Environmental Conservation set 10 µg/L as the water quality standard for petroleum hydrocarbons, water soluble petroleum pollutants in concentrations of 100 µg/L or higher 100 µg/L may cause acute effects on some organisms (Latimer, *et al.,* 1998) and then the human health risks posed. The concentration of DDPH in Alexandria coastal area were also above the risk-based removal level which stated that petroleum products are major pollutants responsible for ecological damage in surface water and the lethal effect of oil concentration occurs in the range (1-10 ug/L), while sub-lethal effect occurs at very low concentrations (0.1-1.0 ug/L) (Hanan, 2007). Among the sub- lethal effects of oil contents are extremely toxic to phytoplankton especially in bay area where concentration of both oil photo-planktons tends to accumulate (Omayma, *et al.,* 2014). Nevertheless, these data suggest that the level of petroleum hydrocarbons is higher than the level fixed by meteorology and Environmental Protection Administration, (MEPA, 1982). It is generally stated that water could be considered polluted when the hydrocarbon concentration is higher than (2.0 ug/L). Petroleum products are major pollutants responsible for ecological damage in surface water. This deposition attracts a huge public concern as the on-going recreational activities on beaches get seriously affected, which in turn affects the tourism industry, and Alexandria Government is concerned about this environmental problem. A comparison of concentrations observed for the study area with other surface waters of the world Figure 3. The DDPH concentrations of Alexandria coast were much higher than those reported for the others Levels as compared to be substantially higher than those from the selected pristine environments such as Arabian Gulf, Saudi, Arabia coast, which recorded values 0.89 µg/L by (Ehrhrdt, *et al.,* 1993); Western Coast of the Philippines, Thailand 1.470 µg/L by (Suriyan, *et al.,* 1998); Saudi Red Sea, Jeddah, Saudi Arabia, 1.572 µg/L by (Sultans, et al., 1997); Suez Canal, 2.1 µg/L, by (El-Samra, *et al.,* 1983). Moreover, (El-Agroudy, *et al.,* 2001; Nagla, 2006; Hanan, 2007) represent values 14.8, 4.387 and 139 µg/L in Suez Gulf, also Mediterranean Sea, Damietta - Man Zalah Lake recorded 3.9 µg/L by (Mohamed, Abd-EL-Hakem 2004). Suez Canal and Arabian Gulf, Saudi - Arabia coast show111 µg/Lby (El-Samr, *et al.,* 1986), and 28.66 µg/L for Red Sea, Suez Canal by (Shereet, 2009), in addition to Red Sea, Saudi Arabia Coast which reverse values174 and 147.2µg/L by (Awad, 1988 & 1990), beside, (Moonkoo, *et al.,* 2013) in west coast of Korea recorded 732 µg/L, (Márcia, *et al.,* 2003) explained 17.9 µg/L in King George Island, Antarctica - Admiralty Bay. In spite of this

shown for locations known to be chronically contaminated by oil, above all, Mediterranean Sea recorded values 5608, 5332, 7449 µg/L by (Maged, *et al.,* 1999; Abd-el Rahman, *et al.,* 2001&2012), However (Mohamed, 2012) display values 11900.857 µg/L in winter and 5376.143 µg/L in summer beside, (Eman, 2013) 15342.375, 34455.25 µg/L for winter and summer respectively, these values are nearly comparable or higher than the study area for Suez Gulf. By compared to other regions of the world, levels are shown to be substantially higher than those from selected pristine environments at all the stations, the concentration of DDPH was greater than the natural background limit No. 4 /1994 (50 µg /L). This finding indicates that coastal areas and semi-enclosed marine, like embayment and harbors, have higher levels of petroleum contamination in water as compared to the open sea areas since the biggest contributions of oil come from terrestrial sources (National Research Council, 1985).
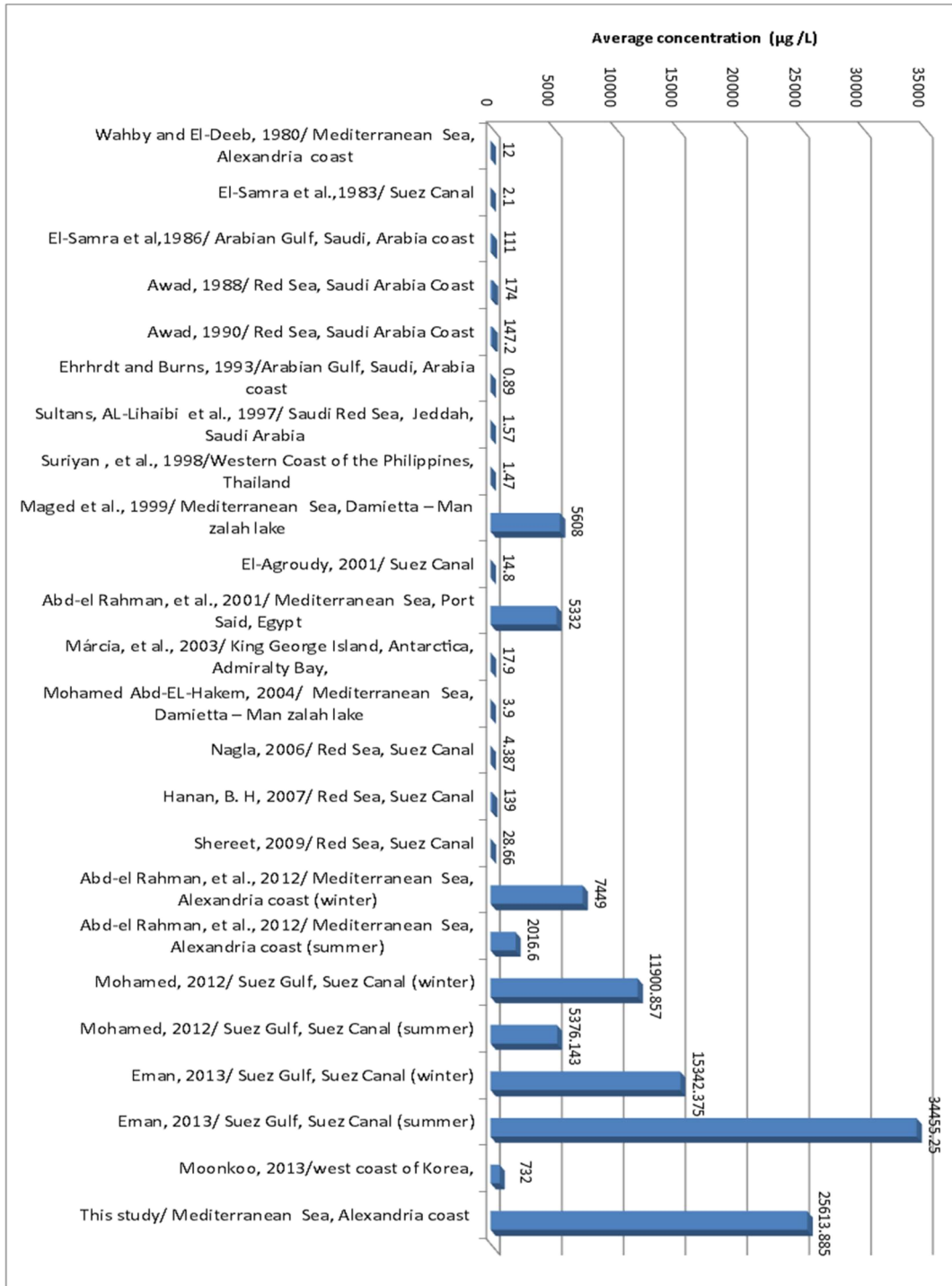
Gas chromatographic analysis (GC)

GC-profiles and pollutant origins

Chromatographic profiles of the aliphatic fraction showed generally the presence of nC$_{10}$ to nC$_{40}$ n-alkanes Figures 4 & 5 and classified into two profiles, represent the different hydrocarbon origins mainly petrogenic, mixed petrogenic and biogenic and finally biogenic hydrocarbons. These types are displayed by samples 11, 10, 13 &3 (beaches) and 4&5 (harbors) each of them were dominance by the odd carbon n-alkanes (C$_{17}$, C$_{19}$, C$_{25}$, C$_{29}$ and C$_{31}$). The first profile were displayed by samples 11, 10, 13 & 3 called slightly weathered profile which exhibit that water samples similar to those obtained for weather petroleum profiles which are consisting of a number of peaks, representing abundant peaks over a wide n-alkanes range starting from nC$_{10}$ up to nC$_{40}$. These n-paraffins are starting out at equal distance above a relatively low envelope of unresolved compounds (UCM). The UCM is believed to be a mixture of structurally complex isomers and / or existence of homologs of branched recycled hydrocarbons that cannot be resolved by capillary columns (Maged, *et al.,* 1999). The presence of two isoprenoid alkanes (pristane and phytane) is well resolved. The striking feature of the GC patterns for stations (11, 10 &13) Figure 4 is the bimodal n- alkane distribution significant for tanker washings (mixed crudes). The most abundant alkanes found in all samples were nC$_{17}$ nC$_{27}$, nC$_{29}$, nC$_{31}$ and nC$_{33}$ which are synthesized by marine algae and higher plant waxes (Saida, *et al.,* 2011). Beside, these samples have a relatively low hydrocarbon content in the lower boiling n-alkanes (nC< 25) rang due to the different weathering processes mainly vaporization, photo-oxidation, dissolution and biodegradations on low molecular weight alkanes. The second profile Figure 5 was highly weathered profile which represented by samples 4&5 show more weathered crude oil profile with abundant n-alkane peaks especially in the range nC$_{16}$ up to nC$_{40}$. It is noted that large envelope of unresolved complex mixture (UCM) and a predominant peak C$_{32}$ n-paraffin at most samples which probably indicative to ballast water is shown at the point near ships waiting zone outside the harbors were the major chromatographic feature observed in this group of samples, this pattern represents typical petrogenic origin (Maged, 1995). This is revealing that there are always a continuous oil inputs in the harbors.

Distribution of Aliphatic and alicyclic hydrocarbons

Alexandria is goods traffic and the most populated city in Egypt along the Mediterranean Sea, and thus generates important industrial, shipping, nautical and tourism activities. Hence, the coastal studied area is exposed to numerous potential sources of contamination such as urban and industrial wastes, petroleum inputs and atmospheric depositions from transports, pyrogenic residues, and industrial and harbor activities. A number of data are available about the distribution of hydrocarbons in the surface water from neighboring coastal areas. Total concentrations of the aliphatic and alicyclic hydrocarbons, unresolved compounds and n-alkanes from C$_{10}$ to C$_{44}$ as well as the individual isoprenoid hydrocarbons, pristane and phytane, and diagnostic criteria used for origin identification are given in Table 3. Total n- alkane concentrations vary from 73.0188 and 99.8890 µg/L. This concentration range generally typifies low polluted to highly pollute coastal and/or open sea water (Volkman, *et al.,* 1992). Figures 4&5 shows examples of GC traces of aliphatic and alicyclic hydrocarbon distribution, representative of the various zones in the Alexandria coastal area, harbor stations 4 and 5; 26-July beach; station 3, Zahra El-A Gamy, 6-October beach and Sidi Krier beach. Of note hydrocarbons have different contributions from both petogenic and biogenic / aquatic and terrestrial sources. The identification of the homologous n-alkanes allows the determination of unresolved complex mixture and maximum for major five constituents in each sample set, which supports evidence for relative incorporation of the different aliphatic hydrocarbon sources. The most of n-alkane distribution patterns show a C max at C$_{25}$, C$_{27}$, or C$_{29}$, and C$_{31}$, some n-alkane distribution patterns are characterized by slight predominance with a C max at C$_{24}$ as observed in Table 3 and Figures 4&5. This feature can be attributed to marked bacterial activities (Qiu, *et al.,* 1991). While, the chromatographically resolved compounds, an unresolved complex mixture (UCM) of branched and cyclic hydrocarbons eluting between nC$_{14}$ and nC$_{40}$, is present for all samples Figures 4&5, this UCM has a maximum

concentration of 91887µg/L for station 3 and minimum 3461.6 µg/L for station 12 which confirms widespread traces of a petroleum origin in all the area (Aboul-Kassim, *et al.,* 1996). Such presence of UCM is the sign of a petroleum input and/or the presence of biodegraded complex mixture of hydrocarbons; and is considered to occur as a result of many coelutions of structurally complex isomers and homologues of branched and cyclic hydrocarbons (Gough, 1990; Kanzari, *et al.,* 2014).

Fig. 3: Comparison between concentrations median of petroleum hydrocarbons in surface seawater (µg / L) by various areas in the world
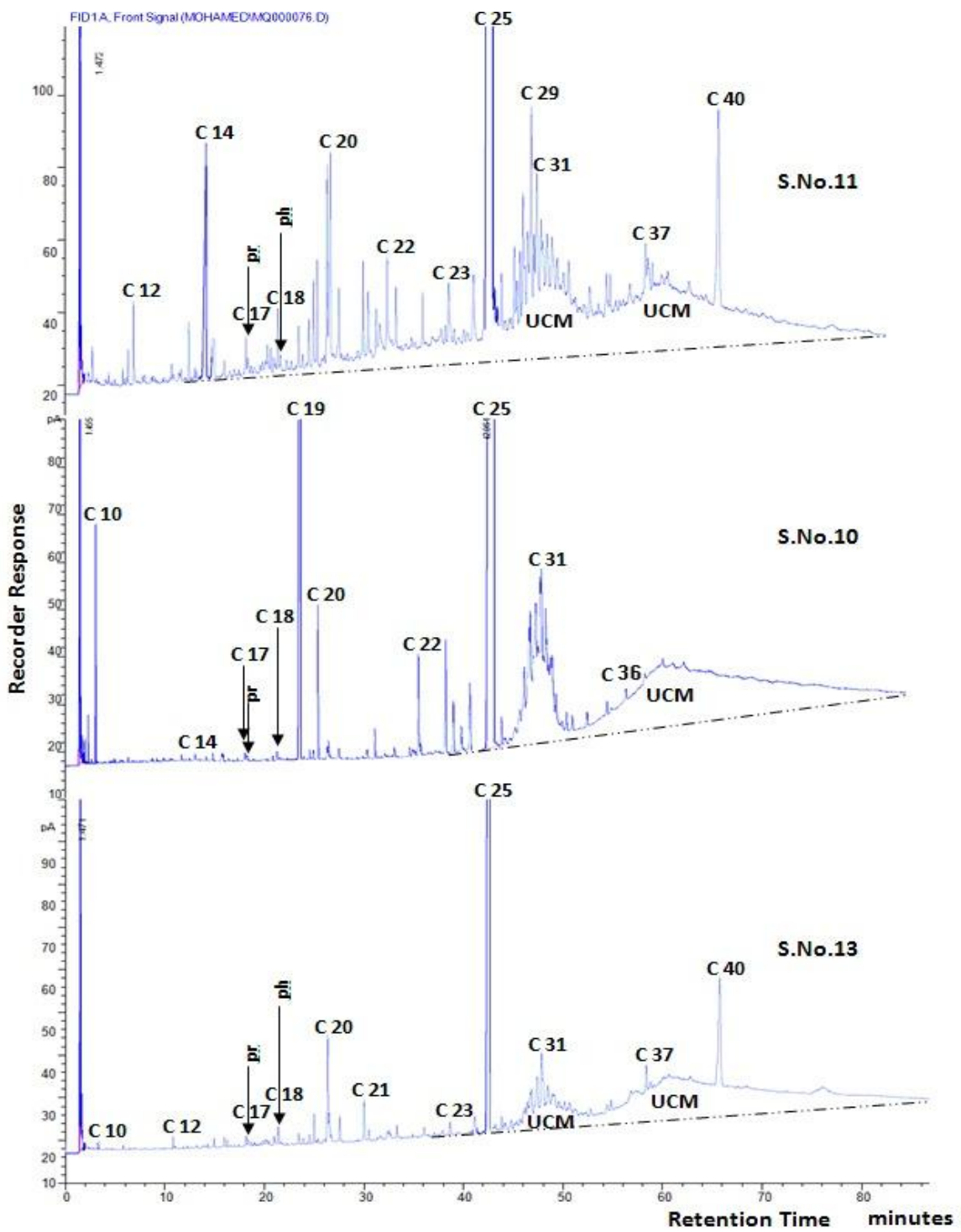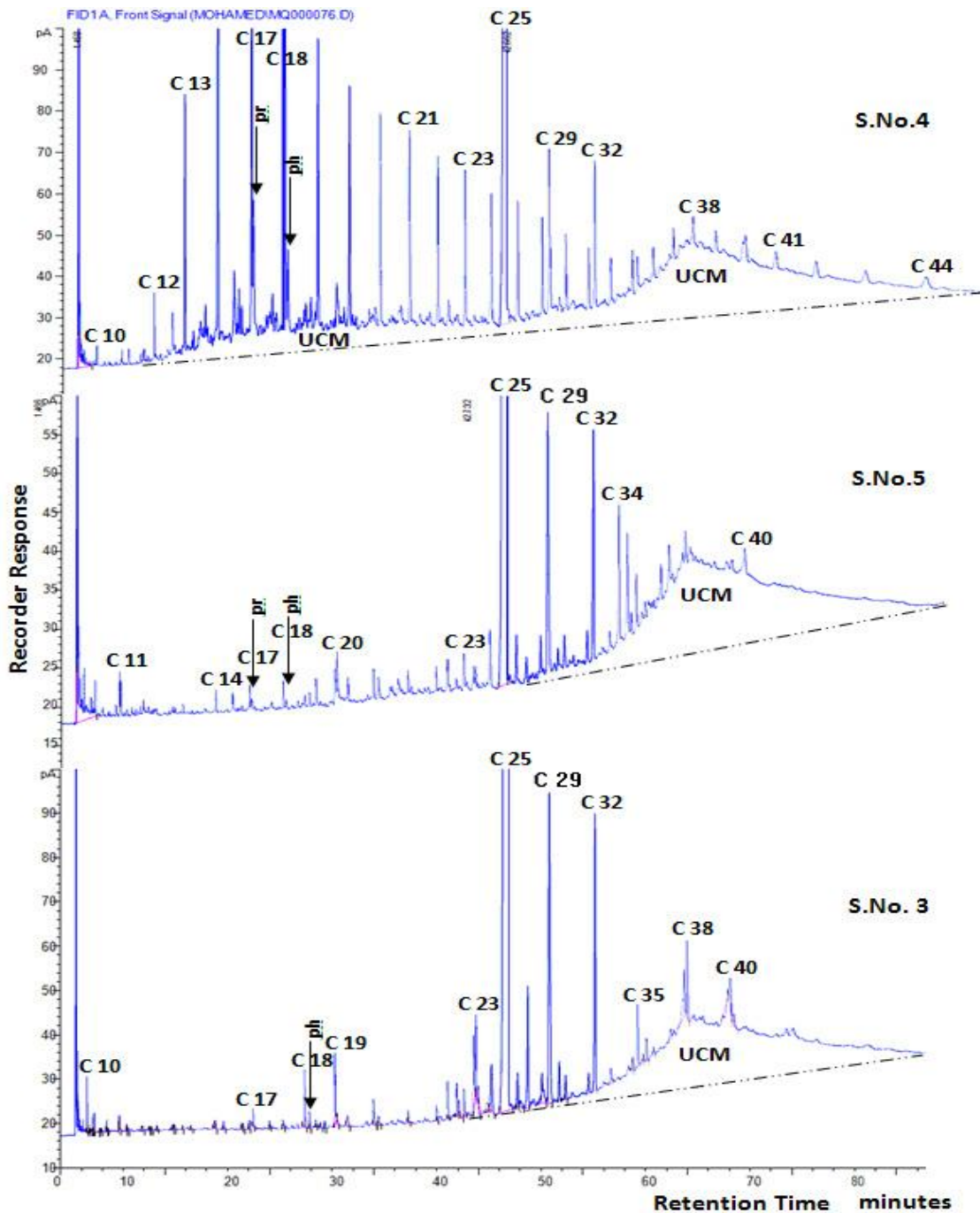
Fig. 4: Gas chromatographic profiles of oils extracted from some selected water samples as an example of GC- analysis

Fig. 5: Gas chromatographic profiles of oils extracted from some selected water samples as an example of GC-analysis

The isoprenoid hydrocarbons pristane (2, 6, 10, 14- tetramethylpentadecane, Pr) and phytane (2, 6, 10, 14-tetramethylhexadecane, Ph) are commonly present in crude oils, usually as major constituents among a much wider distribution of isoprenoid alkanes. Thus they are often considered as good indicators of petroleum contaminations (Volkman, *et al.,* 1992). However, a high concentration of pristane may reflect a zooplankton contribution (Blumer, *et al.,* 1963), while phytane is practically absent in uncontaminated recent surface sea waters (Volkman, *et al.,* 1992). The common isoprenoid alkanes pristane nC_{19} and phytane nC_{20} are present in most petroleum, usually as major constituents. Even though the pristane and phytane are degradable (Le Dreau, *et al.,* 1997), they have been used as indicators of weathered petroleum residues (Tran, *et al.*, 1997). Phytane originates from petroleum hydrocarbons, but pristane can be generated by biogenic processes in the absence of

pollution due to petroleum hydrocarbons. Hydrocarbons in the surface sea water should have a biologic and petrogenic origin. Alexandria area recorded the highest concentrations for nC_{17} (2.3045); nC_{18} (2.0954) and display that both of pristane and phytane ranging from N.D. to 1.3128 µg/L and N.D. to 0.9074 µg/L respectively in station 4 Table 3. The chromatogram obtained appears that all stations except stations 11 and 4, the low molecular weight (LMW, sum of nC_{10} to nC_{20}) ranged from 0.1366 -9.897 µg/L where, the high molecular weight (HMW, sum of nC_{21} to nC_{35}) between 31.780 - 99.190 µg/L, Figures 4&5. The concentrations of nC_{10} to nC_{20} hydrocarbons were lower than the longer chain (>20) n-alkanes (Gokdeniz, *et al.*, 2012), may be due to the evaporation which is generally observed for low molecular weight hydrocarbons (LMW).

Aliphatic biomarkers and origins in polluted sites

The general feature of the aliphatic in the studied samples is: high n-alkanes and isoprenoids concentration, a significant UCM Table 4, very low content of light n-alkanes $<nC_{20}$ in most samples, predominance of nC_{17}; $n C_{19}$ & $n C_{21}$ in the low molecular range nC_{25}; $n C_{27}$; nC_{29} & $n C_{31}$ in the high molecular range Figures 4&5 for examples of chromatograms of the aliphatic fraction. $\leq nC_{14}$/T.n. alkanes, this ratio reverse very low values ranged between 0.0008 - 0.6628 µg/L, due to the loss of the major part of low molecular weight paraffins by dissolution, evaporation and photo-oxidation. $> nC_{14}$ / T.n. alkanes ratio Table 4, contrary by compared with the first ratio show values between 0.3372 and 1.00 µg/L, due to the loss of light fraction from the pollutants samples and relatively low biodegradation weathering of the heavier fractions. Moreover, both of $\leq nC_{17}$/T.n. alkanes and $>nC_{17}$/T.n. alkanes ratios exhibit very low values <1 indicating that different weathering processes dissolution; evaporation; photo-oxidation and biodegradation have greatly affected these oils (Paul, *et al.*, 1982). The higher range $>nC_{17}$/T.n. alkanes ratio have greatly higher values relative to lower range which less affected by weathering. Whereas, Tn.alkanes / Tiso. Alkanes ratio, is often used to indicate degree of biodegradation and weathering, because n-alkanes are more liable to be degraded compared with iso-alkanes (Wang, et al., 1995; Abd El Rahman, *et al.*, 2001). Data presented in Table 4, show values between 2.6314-106.095µg/L. Sample 7(2.6314µg/L) exhibits the least value being relatively more biodegraded as a result exposure to different factor on the other hand, samples 1(106.095 µg/L); 9 (899.909 µg/L); 2(171.280 µg/L) and 12(140.973 µg/L) respectively, as they are less biodegraded compared with the other samples. $n C_{15}$-nC_{25} / nC_{17}-nC_{25} ratio this ratio may be used to indicate addition of algal biosynthesized hydrocarbons and /or degree of weathering. Data obtained Table 4 generally exhibits close values near to (1.00), (Abd El Rahman, *et al.*, 2001) denoting the weathering effects. On the other hand to express the extend of weathering by evaporation and dissolution of low molecular weight- alkanes by using the weathering ratio WR: ΣnC_{23}-nC_{34} / ΣnC_{11}-C_{22} (Nagla, 2006) which increase by increasing weathering. The high values of this ratio at stations 9 (434.988), 1(268.139); 2(1885.498); 3(107.552); 5(98.184) and 6(89.282) Table 4 show that they have undergone severe weathering compared with other samples which have approximately, comparable weathering ratios, these ratios ranged from 3.808-32.588 for the rest of samples. Pristane (Pr) and phytane (Ph) are the two most abundant isoprenoid hydrocarbons and are identified in all samples of this study. These two compounds are considered to originate primarily from the phytyl side chain of chlorophylls during diagnosis. In uncontaminated recent polluted waters, phytane is practically absent and high pristane content can be derived from zooplankton and some other marine animals (Blumer, *et al.*, 1963; Volkman, *et al.*, 1992), leading to the pristine / phytane (Pr/Ph) ratio higher than 1, (Steinhauer, *et al.*, 1992). A Pr/Ph value close to or lower than 1 suggests petroleum contamination (Burns, *et al.*, 1982).

The Pr/Ph ratios obtained for Alexandria surface sea waters are between N.D. and 1.7980 µg/L with an average value, 0.7885 µg/L indicating petroleum contamination Table 4, comparing Pr/Ph ratio obtained from the studied samples with reference crude oils in Ras Garb Egypt, (0.82 µg/L); Qatar marine (1.33 µg/L); Ramadan Egypt, (0.94 µg/L); Marine Bellaim Egypt, (0.84 µg/L); July Egypt, (1.22 µg/L); Es. Sider Libya, (0.89 µg/L); Kuwait (1.63 µg/L); Khafji Iran, (1.78 µg/L); Iranian Light (1.16 µg/L) and Fuel oil (0.78 µg/L) (Abd El Rahman, *et al.*, 2001), good correlations through this ratio can be obtained between Iranian Light (1.16 µg/L) and S.NO.11 (1.0955 µg/L) in addition, Kuwait (1.63 µg/L) and both of samples 5(1.626 µg/L) & 7(1.646 µg/L) also, Khafji Iran, (1.78 µg/L) and S.NO.1 (1.7980 µg/L) Table 4. In addition to their use as petroleum contamination markers, pristane to n. heptadecane (Pr/nC_{17}) and phytane to n. octadecane (Ph/nC_{18}) ratios are often used for evaluating the extent of biodegradation on oils (Commendatore, *et al.*, 2004). Comparatively, isoprenoid hydrocarbons are more resistant to biodegradation than n-alkanes, leading to the increase of Pr/ nC_{17} and Ph/nC_{18} ratios to a value of much higher than 1 when they have been deeply degraded (UNEP, 1995; Hwang, *et al.*, 2002). Petroleum contamination in surface sea water is relatively fresh because, as shown in Table 4, Pr/ $nC17$ and Ph/$nC18$ ratios are around 1. The distribution of Pr/nC17, Ph/nC18 and Pr/Ph ratios for all samples points to a common petroleum contamination source in Alexandria coastal area, Table 4. The carbon preference index (CPI) is a parameter that has frequently been used as a source indicator of n-alkanes in marine aquatic (Colombo, *et al.*, 1989). Ratio Values of cyclic + naphthenic compounds UCM % to total alkanes R % (U/R) vary from 0.0454 and 1.047 µg/L with marked series values Figures 4&5. Such values are in agreement

with the criterion of petroleum contamination proposed by (Maged, *et al.,* 1999) for the presence of dispersed oils from recent oil inputs. Such contamination is higher for samples close to the coast which receive directly sewage/storage tanks pollution/ petrochemical inputs for northern and westerns part of the coast.

This contamination is confirmed by the characterization of biogenic biomarkers (Seifert, *et al.,* 1979). It is also noted that the pattern of chromatograms varies according to the position of the station Figures 4&5. Contamination is evidently low for stations far from coastal pollution sources. The CPI (C_{14}– C_{20}) range for aliphatic hydrocarbons of non siliceous plankton origin were greater than 1 (Youngblood, *et al.,* 1973), data in Table 4 exhibit relatively higher values ranging from N.D.-10.538 µg/L with an average of 2.069 µg/L which confirms biogenic addition (Farrington, *et al.,* 1977) probably due to plant detritus from agriculture drainage, careful examination of CPI data in this range (C_{20}– C_{24}), reverse values ~1 which illustrate petrogenic influence, (Aceves, *et al.,* 1993). Whereas, CPI (C_{26}– C_{35}) range, most of water samples have values failing in the range of 0.3891- 1.4108 µg/L while S.NO.6 (3.3419 µg/L) which denoting biogenic addition. ΣLMW//HMW *n*-alkanes (when $\geq$ 2) and UCM / Σ *n*-alkanes (when > 2), confirm petroleum origin in 4(0.1957) and 7(2.031) Table 4, nC_{17}/nC_{29} and TAR were however, suggesting the biogenic contribution in sites 4(1.669), 5(0.5909) and 8(0.6987), (Zrafi, *et al.,* 2009). The nC_{17}/nC_{29} ratio indicates the relative presence of allochthonous and autochthonous hydrocarbons in the samples; this confirms the limited contribution of marine origin and their dominance at S.NO. 4(1.669), in fact nC_{29} is abundant in plants detritus from agriculture drainage and nC_{17} is dominant in marine organisms. The terrigenous/aquatic TAR and nC_{17}/nC_{29} were however, suggesting the biogenic contribution in the most of the studied area. The terrigenous/aquatic ratio (TAR), which reflects the long-chain *n*-alkane (nC_{27} + nC_{29} + $n\,C_{31}$) to short-chain *n*-alkane (nC_{15} + nC_{17} +nC_{19}) ratio, confirms the importance of terrigenous and aquatic inputs; (Zrafi, *et al.,* 2013; Will, 1995). The TAR ratio Table 4 was higher than 1 at samples 3(1.340); 5(1.017); 10 (1.650); 11(1.202); 13(1.296), but was near the unit for the stations 1(0.9838); 9(1.000); 12(0.9882).

Table 3: Aliphatic hydrocarbons: concentrations (µg/L) of *n*-alkane; individual concentrations of the isoprenoid hydrocarbons pristane and phytane**;** Unresolved complex mixture; Low and high molecular weight; Major five constituents

S.NO.	Range of T*n*. Alk.	T*n*. lk.	*n*C$_{17}$	Pr	*n*C$_{18}$	Ph	UCM	LMW	HMW	Major five constituents %
1	nc_{10}-nc_{38}	99.0663	0.0353	0.0456	0.0254	0.0218	43879.7	0.3450	96.240	(C$_{25}$) 78.038; (C$_{29}$) 1.086; (C$_{31}$) 0.811;(C$_{34}$) 0.749; (C$_{24}$) 0.257
2	nc_{10}-nc_{40}	99.4196	N.D.	N.D.	N.D.	N.D.	7821	0.1366	99.190	(C$_{25}$) 48.182; (C$_{24}$) 0.092; (C$_{26}$) 0.073; (C$_{33}$) 0.066; (C$_{27}$) 0.055
3	nc_{10}-nc_{40}	96.8537	0.0354	0.0674	0.2760	0.0795	91887	0.7113	95.187	(C$_{25}$) 69.478;(C$_{29}$) 1.661; (C$_{32}$)1.142; (C$_{27}$) 0.526;(C$_{38}$) 0.319
4	nc_{10}-nc_{44}	73.0188	2.3045	1.3128	2.0954	0.9074	4949	9.897	50.563	(C$_{25}$) 41.897;(C$_{17}$)1.957;(C$_{15}$) 1.800;(C$_{18}$) 1.779;(C$_{19}$) 1.669
5	nc_{10}-nc_{40}	98.1837	0.0722	0.0421	0.0881	0.0259	22871.6	0.5327	80.384	(C$_{25}$) 41.110;(C$_{40}$) 9.205;(C$_{29}$) 0.651; (C$_{32}$) 0.449;(C$_{24}$) 0.156
6	nc_{10}-nc_{40}	97.8076	0.0736	0.0	0.0971	0.0	4587.3	0.7651	96.444	(C$_{25}$) 80.807; (C$_{31}$)1.860; (C$_{24}$) 0.688; (C$_{34}$) 0.586; (C$_{40}$) 0.451
7	nc_{10}-nc_{40}	97.3684	0.1153	0.0811	0.1324	0.0492	4747.5	65.379	31.780	(C$_{10}$) 55.029;(C$_{25}$) 25.632; (C$_{20}$) 0.268; (C$_{29}$) 0.194; (C$_{33}$) 0.139
8	nc_{10}-nc_{40}	94.8805	0.2909	0.1973	0.3740	0.1312	2682.1	2.660	91.698	(C$_{25}$) 57.095;(C$_{20}$) 0.384;(C$_{18}$) 0.239;(C$_{15}$) 0.206; (C$_{40}$) 0.204
9	nc_{10}-nc_{36}	99.8890	N.D.	N.D.	N.D.	N.D.	8810.1	0.2288	99.605	(C$_{25}$) 66.055;(C$_{32}$) 0.417; (C$_{34}$) 0.192; (C$_{24}$) 0.152; (C$_{10}$) 0.111
10	nc_{10}-nc_{37}	99.3789	0.0171	N.D.	0.2274	N.D.	14506.6	7.536	91.754	(C$_{25}$) 60.252;(C$_{19}$) 4.424;(C$_{20}$) 0.295(C$_{23}$) 0.254;(C$_{24}$) 0.2276
11	nc_{10}-nc_{40}	95.1012	0.1231	0.0536	0.1821	0.0489	1377.46	3.417	89.783	(C$_{25}$) 68.772; (C$_{14}$)1.167 (C$_{29}$) 0.622; (C$_{20}$) 0.560; (C$_{30}$) 0.411
12	nc_{10}-nc_{40}	99.2956	0.0064	0.0083	0.0025	0.0129	3461.6	4.490	99.163	(C$_{25}$) 90.809; (C$_{19}$) 3.961;(C$_{20}$) 0.375;(C$_{24}$) 0.313;(C$_{23}$) 0.065
13	nc_{10}-nc_{40}	95.7980	0.1524	0.1038	0.0944	0.2340	6096.5	2.374	89.107	(C$_{25}$) 53.727; (C$_{40}$) 2.424;(C$_{31}$) 0.919;(C$_{20}$) 0.763;(C$_{29}$) 0.392

*Tn- alkanes: The sum of total n-alkanes from (nC$_{10}$ to nC$_{40}$); Isoprenoids **(pr):** pristane and **(ph):** phytane; UCM: Unresolved complex mixture; LMW: Low molecular weight Σ nC$_{10}$ to nC$_{20}$; HMW: High molecular weight Σ nC$_{21}$ to nC$_{35}$ **(Gokdeniz, et al., 2012); Major five constituents:** The five n-alkanes with a maximum concentration; **N.D.:** Under the limit of detection.*

Ultraviolet spectroscopy technique

The UV spectra for all oil extracted from Alexandria coastal area have the same basic feature Figure 6. Most samples have a shoulder band at 287 nm. This denotes different aromatic classes are present in the extracted oil. The recommended four absorption bands ratios (Henning, *et al.,* 1979) were calculated from spectra in Table 5. The first ratio 205/215 has low values ranging between 0.7002 and 1.4715. Good agreement between S.NO.1 (1.3608), 2(1.3563) and 9(1.4715) in this range indicates that low molecular samples have nearly identical aromatic values. Normally, light fractions of petroleum hydrocarbons have higher solubility in water and high volatility. As a result fractions which include benzene, xylenes and toluene are seriously affected especially by evaporation, (Neveka, *et al.,* 1990). Correlating the data for the first ratio, it is clear that most of the studied samples have higher values with respect to other ratios which confirm that the light fractions form mono-aromatic hydrocarbon are freshly oil spill. The second ratio 228/256 has generally higher values relative to the other two ratios 248/267 and 248/278. This ratio 228/256 has been taken as a good parameter for petroleum input and is constant for particular oil, but varies for different oils; it is independent on the concentration of oils, and the data have small variations indicating few oil origins, (Levy, 1980). The data for the last two ratios reveres values generally within the range indicating the different types of di-and poly-aromatic hydrocarbons (Maged, *et al.,* 1999) show good correlations. Finally, the three different aromatic classes which characterized petroleum hydrocarbons are detected in the extracted oils from the surface water taken from studied area. Such compounds if accumulated in lage amounts may cause harmful effects for marine life.

Table 4: Selected ratios recorded for Alexandria coastal sea water

Station / Selected ratios	1	2	3	4	5	6	7	8	9	10	11	12	13
≤ nC_{14}/T.n. alkanes	0.001	0.0008	0.0009	0.0557	0.0014	0.0027	0.6628	0.0072	0.0020	0.0026	0.0207	0.0001	0.0036
> nC_{14}/T.n. alkanes	1.000	0.9983	0.9991	0.9937	0.9993	0.9973	0.3372	0.9954	0.9981	0.9974	0.9793	0.9999	0.9964
≤ nC_{17}/T.n. alkanes	0.0026	0.0013	0.0015	0.0784	0.0028	0.0035	0.6655	0.0143	0.0020	0.0008	0.0235	0.0003	0.0040
> nC_{17}/T.n. alkanes	0.9974	0.9983	0.9985	0.9217	0.9972	0.9965	0.3345	0.9857	0.9980	0.9992	0.9765	0.9997	0.9984
Tn.alk. / Tiso.alkanes	106.095	171.280	30.783	2.703	54.031	44.614	2.6314	18.3186	899.909	159.997	19.4130	140.973	22.798
nC_{15}-nC_{25}/ nC_{17}-nC_{25}	1.016	1.000	1.00003	1.049	1.0009	1,000	1.0013	1.004	1.000	1.0004	1.0016	0.9999	1.0027
WR: Σ nC_{23}-nC_{34}/Σ nC_{11}-C_{22}	268.139	1885.498	107.552	3.808	98.184	89.282	24.570	32.588	434.988	11.834	21.977	20.822	28.086
Pr/Ph	1.7980	N.D.	0.0471	1.447	1.626	N.D.	1.646	1.5036	N.D.	N.D.	1.0955	0.6429	0.4438
Pr /nC_{17}	1.292	N.D.	1.9018	0.5697	0.583	N.D.	0.0911	0.6783	N.D.	N.D.	0.4353	1.3071	0.6812
Ph /nC_{18}	0.8580	N.D.	0.2881	0.4330	0.294	N.D.	0.3720	0.3509	N.D.	N.D.	0.2686	5.1230	2.4788
Wt % cyclic + naphthenic compounds (UCM%)	17.824	51.137	22.276	15.090	46.694	11.390	14.592	36.081	32.795	23.515	19.430	4.347	35.434
Wt % total alkanes (R %)	82.176	48.863	77.724	84.910	53.306	88.610	85.408	63.919	67.205	76.484	80.570	95.653	64.566
UCM/ R	0.2169	1.047	0.866	0.1777	0.8760	0.1285	0.1709	0.5645	0.4880	0.3074	0.2418	0.0454	0.5488
CPI (nC_{14}-nC_{20})	1.366	0.2185	0.7700	1.2951	0.8938	0.4119	0.3741	0.7305	N.D.	9.666	0.1815	10.538	0.4545
CPI (nC_{20}-nC_{24})	0.3769	0.5288	0.8836	0.5329	0.5079	0.4701	0.4283	1.1824		0.4350	0.4188	0.1041	0.4874
CPI (nC_{26}-nC_{35})	1.218	0.6217	1.429	0.8548	1.0625	3.3419	1.1654	1.0025	0.8875	0.3891	0.9937	1.4108	1.3107
LMW/HMW	0.0036	0.0014	0.0075	0.1957	0.0066	0.0079	2.031	0.0290	0.0023	0.0821	0.0381	0.0452	0.0266
UCM / Σn.alkanes	78.947	125	948.720	68.393	232.947	46.901	48.758	28.268	88.199	145.973	14.484	34.862	63.639
TAR	0.9838	N.D.	1.340	0.333	1.017	2.933	0.7802	0.3155	1.000	1.650	1.202	0.9882	1.296
nC_{17}/ nC_{29}	0.0267	N.D.	0.0166	1.669	0.5909	0.07554	0.5077	0.6987	N.D.	0.1840	0.1592	0.06315	0.6078

≤ nC_{14}/T.n. alkanes: Σ n-alkanes ≤ nC_{14} to total n-alkane; > nC_{14}/ T.n. alkanes: Σ n-alkanes> nC_{14} to total n-alkanes; ≤ nC_{17}/T.n. alkanes: Σ n-alkanes ≤ nC_{17} to total n-alkanes; > nC_{17}/T. n. alkanes : Σ n-alkanes > nC_{17} to total n-alkanes; Tn.alk. / Tiso. alkanes: The sum of total n-alkanes to the sum of total iso.alkanes; nC_{10}-nC_{25}/ nC_{17}- nC_{25}: normal alkanes from nC_{10}-nC_{25} over normal alkanes from nC_{17}- nC_{25}; WR: weathering ratio = (sum nC_{23} – nC_{34} /sum nC_{11}– nC_{22}); Pr/Ph: pristane (Pr) over phytane (Ph) ratio; Pr /nC_{17}: pristane to carbon number nC_{17}; Ph /nC_{18}: phytane to carbon number nC_{18}; Wt % cyclic + naphthenic compounds (UCM %): Unresolved complex mixture; w% total alkanes (R%): resolved aliphatic hydrocarbon; UCM/R: Unresolved complex mixture over resolved aliphatic hydrocarbon; LMW/HMW: the ratios of low molecular weight Σ nC_{10} - nC_{20} to high molecular weight ΣnC_{21} to nC_{35}; CPI nC_{14}-nC_{20}, odd to even carbon preference index from nC_{14} tonC_{20}; CPI nC_{20}-nC_{24}, odd to even carbon preference index from nC_{20} to nC_{24}; CPI nC_{26}-nC_{35} odd to even carbon preference index from nC_{26} to nC_{35}; TAR : Terrigenous/aquatic ratio calculated as (nC_{27} + nC_{29} + nC_{31}) / (nC_{15} + nC_{17} + nC_{19}), **(Bourdonniere, et al., 1996); N.D. :** Under the limit of detection.

FT-IR Technique

This technique was used by (Literathy, *et al.,* 1989) for characterization of petroleum and its degradation compounds dissolved or dispersed in sea water; Table 6 and Figure 7 reveals that the characteristic band at 2957 cm^{-1} is due to asymmetrical stretching mode of vibration C-H$_3$ bands. Strong bands at 2926and 2852 cm^{-1} due to stretching vibration of methylene groups (δ_{as} CH$_2$) and (δ_s CH$_2$) respectively, (Zhengzhen, *et al.,* 2013). Strong bands at 1462 cm^{-1} due to (δ_{as} CH$_3$) bending vibration of CH$_3$ group and medium band at 1381 cm^{-1} due to (δ_{as} CH$_3$) bending of CH$_3$ groups, (Abd El Rahman, *et al.,* 2001). Strong band at 1729 cm^{-1} most likely due to the presence of carboxylic esters, also the spectra depict sharp band at 1049 cm^{-1} significant to carbohydrates C-O stretch, (Yanan, *et al.,* 2010) beside, medium band at 802 cm^{-1} was significant for naphthenic compounds, (Keroly, *et al.,* 2013). In addition to medium band at 742 cm^{-1} due to out of plane bending of =C-H group in mono and poly-nuclear aromatics.
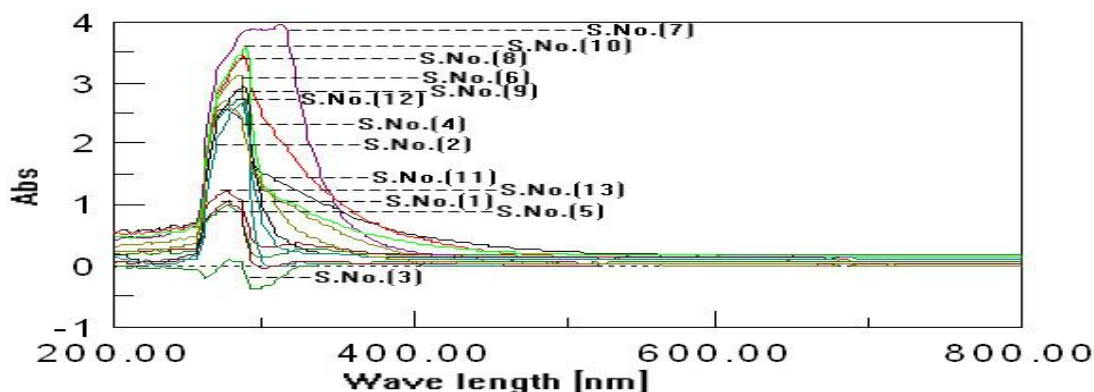

Fig.6: UV absorption spectra for oils extracted from Alexandria coastal sea waters

Table 5: Calculated UV absorption ratios for the oil extracted from Alexandria coastal sea waters

S.NO.	Location	A205/A215	A228/A256	A248/A267	A248/A278
1	EL-Montazah Beach	1.3608	0.4329	0.0994	0.0852
2	Miami Beach	1.3563	0.1073	0.0486	0.0376
3	26-July Beach	0.7002	0.3890	0.5929	0.8138
4	The east port of Alexandria	0.9284	0.5752	0.1387	0.1290
5	The west port of Alexandria	0.9224	0.7015	0.2727	0.2381
6	west port of Aldekhela	0.9861	0.7098	0.1660	0.1398
7	EL-Nikhil Beach	0.9736	0.6615	0.1884	0.1627
8	EL-Bitash Beach	0.9392	0.8170	0.2980	0.1944
9	EL-Hanovill Beach	1.4715	0.1530	0.0692	0.0564
10	Zahra El-A Gamy	0.8828	0.7639	0.2088	0.1741
11	6-October Beach	0.9883	1.3932	0.2704	0.2590
12	Center the drainage A Gamy (km.21)	0.8930	0.2771	0.0457	0.0385
13	Sidi Krier Beach	0.9884	0.7877	0.2520	0.2385

A: Absorbance

Table 6: Infra-Red Signals and Assignments of the oil extracted from Alexandria coastal sea waters

Wave number cm⁻¹	Component shape	Assignments
2957	Strong	Asymmetrical stretching of vibration C-H_3 bands
2926	Strong	Stretching vibration of methylene groups δ_{as} CH_2
2852	Strong	Stretching vibration of methylene groups δ_s CH_2
1729	Strong	Carboxylic esters
1462	Strong	-CH_3 bending
1381	Medium	δ_{as} CH_3 bending of CH_3 groups
1276	sharp	Carboxylic acids
1125	sharp	Two strong, broad bands of trifluromethyl fluoroalkanes
1073	sharp	C-X (ordinary fluoroalkanes) stretching frequency
802	Medium	Naphthenic compounds
742	Medium	=C-H group in mono and poly-nuclear aromatics
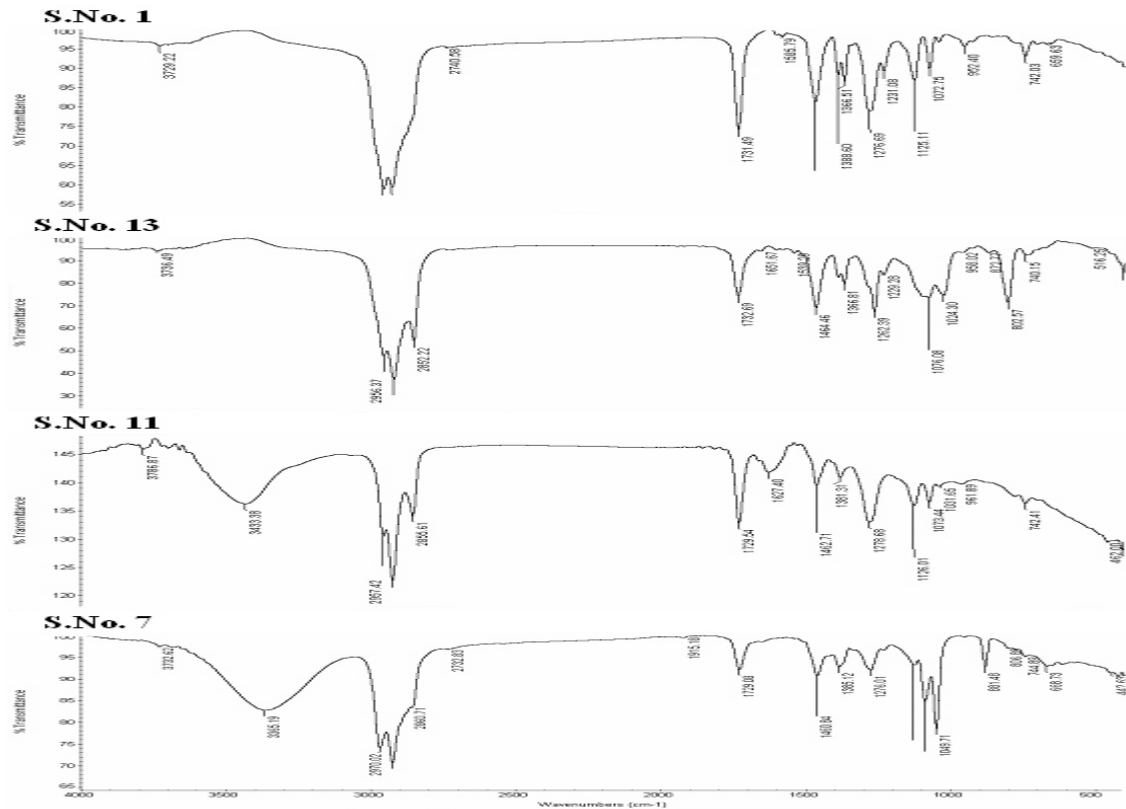
Fig.7: FT-IR absorption spectra for oils extracted from some selected water samples as an example of FT-IR analysis

Conclusion and Recommendations

The level of dissolved /dispersed petroleum hydrocarbons in Alexandria coastal sea waters ranged between 2421 and 183817 µg/L, with a mean value of 25613.885 µg/L. A comparison of mean concentrations for Alexandria coastal sea water with other regions of the world show that the Egyptian Mediterranean aquatic environment is much higher polluted than various areas in the world and higher than that authorized by the Egyptian law of Environment No. 4 /1994 (50 µg /L). Gas chromatographic analysis of oil extracted from Alexandria coastal seawaters indicates that pollutants' are mainly of petroleum origin in both dissolved and dispersed states. However, some oils have mixed biogenic-petrogenic nature. Low molecular weight alkanes have lost due to the different weathering processes mainly vaporization, photo-oxidation, dissolution and biodegradation. In spite of chronic petroleum pollution, the predominance of nC_{25}, nC_{27}, nC_{29} and nC_{31} alkanes could be used as biological markers in polluted waters. GC parameters such as unresolved / resolved compound ratio, pristane / phytane, carbon preference index, pristane / n.heptadecane and phytane / n-octadecane indicate a petrogenic contamination in the whole area. Spectroscopic studies UV and FT-IR visible reveal a significant contamination by aliphatic and aromatic hydrocarbons with few oil origins. Nevertheless, these data suggest that the level of petroleum hydrocarbons is higher than the level fixed by meteorology and Environmental Protection Administration, MEPA 1982. Petroleum products are the major pollutants responsible for ecological damage in surface water, this attracts a huge public concern as the on-going recreational activities on beaches get seriously affected, which in turn affects the tourism industry, and Alexandria Government is concerned about this environmental problem. So, it must be removal the oils from ballast water before discharging into the sea, Must be decided to restore this important coastal area by stopping the direct discharge of wastewater effluents into the semi-enclosed harbors and coastal areas, then gradually reducing to discharge of the municipal wastewater through marine outfalls. Alexandria Coastal sea waters and some sites in the Mediterranean coast should be included in a monitoring program to allow the detection of future changes. This will contribute to the development of management and control measures to preserve the coastal and marine environment.

References

Abd El Rahman, M., A. F. Nazik, M. S. Maged, E. A. Omyma, 2001. State of Petroleum pollution in the south eastern Mediterranean Sea, Port Said coastal waters. Egypt. J. Petrol., 10, 2:1-14.

Abd El Rahman, M., A. F. Nazik, M. S. Maged, E. A. Omyma, 2012. Contamination of water on Alexandria seashore,15th International Conference on petroleum Mineral Resources and Development 8-10 April, Cairo, Egypt.

Aboul-Kassim, T., B. Simoneit, 1996. Lipid geochemistry of surficial sediments from the coastal environment of Egypt I. Aliphatic hydrocarbons - characterization and sources. Marine Chemistry, 54: 135–158.

Aceves, M., J. Grimalt, 1993. Gas chromatographic screening of organic compounds in urban aerosols: II, Changes in hydrocarbon composition during storage. Original Research Article. Journal of chromatography, 655: 133-140.

AWAD, H., 1988. Potential and causes of accidental oil spills in the Red Sea and Gulf of Aden: 1974-1986, a review. Bulletin of the National Institute of Oceanography & Fisheries, Egypt, 14, (1): 293-296

AWAD, H., 1990. Hydrocarbon content in Red Sea surface waters and fishes in the region between Jeddah and Yanbu, Saudi Arabia. In: Proceedings of the First Conference on Environmental Sciences, 27-31 January 1990, Sabha, Lybia. In Arabic, English abstract.

Blumer, M., M. Mullin, D. Thomas, 1963. Pristane in zooplankton. Science, 140–974.

Bouloubassi, I., A. Saliot, 1993. Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers (NAH, LAB, PAH) Oceanol. Act, 16: 145–161.

Bourbonniere, R.A., P.A. Meyers, 1996. Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. Limnol. Oceanogr, 41: 352–359.

Burns, K.A., J.P. Villenuve, V.C. Anderlin, S.W. Fowler, 1982. Survey of tar, hydrocarbon and metal pollution in the coastal waters of Oman Original Research Article. Marine Pollution Bulletin, 13, 7: 240 - 247.

Colombo, J., E. Pelletier, C. Brochu, M. Khalil, J. Catoggio, 1989. Determination of hydrocarbon sources using *n*-alkane and poly- aromatic hydrocarbon distribution indexes, Case study: Rı́o de la Plata estuary, Argentina. Environmental Science and Technology, 23: 888–894.

Commendatore, M.G., J.L. Esteves, 2004. Natural and anthropogenic hydrocarbons in sediments from the Chubut River (Patagonia, Argentina). Marine Pollution Bulletin, 48: 910–918.

Ehrhardt, M.G., K. A. Burns, 1993. Hydrocarbons and related photo- oxidation products in Saudi Arabian Gulf coastal waters and hydrocarbons in underlying sediments and bio-indicator bivalves. Marine Pollution Bulletin, 27: 187-197.

El Samra, M. I., K. Z. El Deeb, A. I. Askar, S. D. Wahby, M. S. El Shazly, 1983. Preliminary study of petroleum hydrocarbon pollution along the Suez Canal, Bull. Nat. Inst. Oceanography & Fish, 9: 97 – 101.

El Samra, M.I., H.I. Emara, F. Shunbo, 1986. Dissolved petroleum hydrocarbon in the northwestern Arabian Gulf, Marine Pollution Bulletin, ISSN: 0025-326X, 17, 2: 65-68

El-Agroudy, N., A. El. Abd allah, 2001. Environmental study on hydrocarbon materials in Suez Canal provides

Eman, M. K., 2013. Thesis submitted for MSC. Physico-Chemical studies on some selected water pollutants. Al-Azhar University.

Farrington, J.W., B.W. Tripp, 1977. Hydrocarbons in western North Atlantic surface sediments Original Research Article, Geochimica ET Cosmochimica Acta, 41: 1627-1641.

Finn, D.P., 1979. Oil pollution from tankers in the Straits of Malacca, East-West Center, Honolulu, Hawaii.

Gokdeniz, N. E, K. Aynur, U. Deniz, A. Oya, D. Enis, U. Esin, K. Filiz, T. Nermin, F. Y.˘ul, 2012. Polycyclic aromatic and aliphatic hydrocarbons pollution at the coast of Aliag˘a (Turkey) ship recycling zone. Marine Pollution Bulletin, 64. 1055–1059

Gough, MA. RJ. Rowland, 1990. Characterization of unresolved complex mixtures of hydrocarbons in petroleum, Nature, 344: 648–50.

Guitart, C., N. Garcia-Flor, J.M. Bayona, J. Albaigés, 2007. Occurrence and fate of polycyclic aromatic hydrocarbons in the coastal surface micro-layer. Mar. Pollut. Bull., 54: 186–194.

Hanan, B., 2007. Thesis submitted for MSc. Assessment of pollution in the marine Environment in Suez Canal. Fac. Sci., Al-Azhar University.

Henning, H.F., 1979. Quantitative analysis of residual fuel oil in sediment samples by absorption spectrophotometer. Original Research Article: 234-237.

Humphrey, B., P.D. Boehm, M.C. Hamilton, R.J. Nostrum, 1987. The fate of chemically dispersed and untreated crude oil in Arctic benthic biota. Arctic, 40: 149-161.

Hwang, R., T. Heidrick, B. Mertani, Li Qivayanti, 2002. Correlation and migration studies of North Central Sumatra oils. Organic Geochemistry, 33: 1361–1379.

Ip standards, 1993, for analysis and testing of, petroleum and related products .

Kanzari, F., A. Syakti, L. Asia, L. Malleret, A. Piram, G. Mille, P. Doumenq, 2014. Distributions and sources of persistent organic pollutants (aliphatic hydrocarbons, PAHs, PCBs and pesticides) in surface sediments, of an industrialized urban river (Huveaune), France. Science of the Total Environment, 478: 141–151.

Keizer, P.D., D.C. Jr. Gordon, 1973. Detection of trace amounts of oil in sea water by Fluorescence spectroscopy. J. Fish. Res. Bd, Can., 30: 1039-1045.

Keroly, A.P., G. P. Colati, E. V. Dalmaschio, A. O. Castro, B. G. Gomesb, W. R. Vaz, 2013. Monitoring the liquid/liquid extraction of naphthenic acids in Brazilian crude oil using electro spray ionization FT-ICR mass spectrometry (ESI FT-ICR MS) Fuel, 108: 647–655.

Latimer, JS, JG. Quinn, 1998. Aliphatic Petroleum and Biogenic Hydrocarbons Entering Narragansett Bay from Tributaries under Dry Weather Conditions. Estuaries, 21: 91–107.

Le Dreau, Y., F. Jacquot, P. Doumenq, M. Guiliano, J.C. Bertrand, G. Mille, 1997. Hydrocarbon balance of a site which had been highly and chronically contaminated by petroleum wastes of a refinery (from 1956 to 1992). Mar. Pollut. Bull., 34: 456–468.

Levy, E.M., 1980, Oil pollution and seabirds: Atlantic Canada 1976–1977 and some implications for northern environments Original Research Article, Marine Poll. Bull, 11: 51-56.

Lipiatou, E., A. Saliot, 1991. Fluxes and transport of anthropogenic and natural polycyclic aromatic hydrocarbons in the western Mediterranean Sea. Mar. Pollut. Bull, 22: 297–304.

Lterathy, P., S. Harder, O. Samhan, G. Mrel, 1989. Experimental Studies on Biological and Chemical Oxidation of Dispersed Oil in Seawater, Water Science Technology, 21, 8-9: 845–856.

Maged, M. S., E. A. Omyma, A. F. Nazik, M. M. Abd El Rahman, 1999. Hydrocarbon contamination in Manzalah Lake water. Egypt. J. petrol., 8 (1), 77-85

Maged, M., 1995. Thesis submitted for Ph.D. Contribution to study of oil in Mediterranean Egyptian environment chemistry Dept. Faculty of Science Ain Shams Univ., Chapter I.: 1-5.

Márcia C. B., Z. L. Eliete, R. W. Rolf, 2003. Four-year survey of dissolved/dispersed petroleum hydrocarbons on surface waters of Admiralty Bay, King George Island -Antarctica Rev. bras. Occanogr. 51(unico): 33-38.

Mazurek, M., B. R. Simoneit, 1984. Characterization of biogenic and petroleum derived organic matter in aerosols over remote, rural and urban areas. In: Keith, L.H. (Ed.), Identification and Analysis of Organic Pollutants in Air. Ann Arbor Science, Boston: 353–370.

MEPA, 1982. Environmental protection standard Document, Meteorology and Environment protection Administration. Saudi Arabia, 17: 1409 – 01.

Mohamed, I.A., 2012. Thesis submitted for MSc. Studied on water quality in selected area of Egypt, AL-Azhar University.

Mohamed, S. A. Abd-EL-Hakem, 2004. Thesis submitted for MSc. Studies on oil pollutants in some selected important Egyptian marine environment, AL-Azhar University.

Moonkoo, K., H. H. Sang, W. Jongho, H. Y. Un, H. J. Jee, Y. H. Sung, G. A. Joon, J. Changkyu, K. Eunsic, M. Gi, S. B. Han, W. C. Hyun, J. S. Won, 2013. Petroleum hydrocarbon contaminations in the intertidal seawater after the Hebei Spirit oil spill e Effect of tidal cycle on the TPH concentrations and the chromatographic Characterization of seawater extract. Water research, 47: 758 -768.

Nagla, M., 2006. Thesis submitted for Ph D. Studied on Pollutants Contaminating Red Sea Marine Environmental with Special Emphasis to Aromatic Hydrocarbons Al-Azhar University, Girls Branch.

National Research Council, 1985. Oil in the Sea-Inputs, fates and effects, National Academy Press, Washington D.C., 601.

Nazik, A. F., E. A. Omayma, M. Abd el-Rahman 2013. Contamination of Water, Sediment, Tar ball and Fishes by Polyaromatic Hydrocarbons (PAHs) in Alexandria Sea Coasts. Journal of Applied Sciences Research, ISSN 1819-544X., 9, 11: 5619-5632.

Nevenka, A., Katica, B. Sertić, R. Nevenka, 1990. Influence of Weathering on Oil Spill Identification. International J. Environmental Analytical Chemistry, 39: 381-390.

Omayma, E. A., A. A. Nabila, A. M. Sawsan, M. D. Mamdouh, 2014. Environmental Assessment of Contamination by Petroleum Hydrocarbons in the Aquatic Species of Suez Gulf, ISSN: 2166-074 Florida, USA. International Journal of Modern Organic Chemistry, 3(1): 1-17.

Osman, A., R. I. Engy, M. Amany, K. Jammo, 2003. Approaches to Environmental restoration of polluted harbor with submerged archaeology: the Alexandria case study. Marine pollution bulletin, 47, Issues 1-6: 193-197.

Paul, D. B., E. B. Judith, L. F. David, A. E. Adria, 1982. A Chemical investigation of the transport and fate of petroleum hydrocarbons in littoral and benthic environments, The TSESIS oil spill Original Research Article. Marine Environmental Resources, 6: 157-188.

Qiu, Y., M. Bigot, A. Saliot, 1991. Non-aromatic hydrocarbons in suspended matter from Changjiang (Yangtse River) Estuary, their characterization and variation in winter and summer (low- and high-flow) conditions. Estuarine Coastal and Shelf Science, 33: 153–174.

Rielley, G., R. Collier, D. Jones, G. Eglinton, 1991. The biogeochemistry of Ellesmere Lake, UK-I: source correlation of leaf wax inputs to the sedimentary Lipid record. Org. Geochem, 17: 901–912.

Saida, B., I. Soumayak, S. Alain, Er. Hassan, 2011. Assessment of the Moroccan Mediterranean Coasts Contamination by hydrocarbon - Non Aromatic hydrocarbons, aromatic hydrocarbons and linear alkyl benzenes. International Journal of Geosciences, 2: 562-572.

Seifert, W.K., J.M. Moldowan, 1979. The effect of biodegradation on steranes and terpanes in crude oils. Geochimica ET Cosmochimca Acta, 43: 111–126.

Sharkawi, F. EL., 1985. Pollution of the beaches of Alexandria due to the discharge of sewage, A case study water science and technology, pollutant of the Mediterranean sea, proc, of an IAWPRC Int Reg conf, split, yugosl: 273-278.

Shereet, S.M., 2009. Pollution of petroleum hydrocarbon in the new Damietta harbor, Egypt. Emirates Journal for Engineering Research, 14, 1: 65-71.

Simoneit, B.R., 1985. Application of molecular marker analysis to vehicular exhaust for source reconciliation. Int. J. Environ. Anal., Chem., 22: 203–233.

Steinhauer, M.S., P.D. Boehm, 1992. The composition and distribution of saturated and aromatic hydrocarbons in near shore sediments, river sediments, and coastal peat of Alaskan Beaufort Sea: implications for detecting anthropogenic hydrocarbon inputs. Marine Environmental Research, 33: 223–253.

Sultans, AL-L., S. AL. Turki, 1997. Petroleum Hydrocarbons in Saudi Red Sea Coastal Waters. JKAU, Mar. Sci., 8: 83-89.

Suriyan, S., W. Gullaya, 1998. Petroleum Hydrocarbon Contamination in Seawater along the Western Coast of the Philippines, Department of Marine Science, Chulalongkorn University, Bangkok 10330, Thailand, Southeast Asian Fisheries Development Center.

Tran, K., C.C. Yu, E.Y. Zeng, 1997. Organic pollutants in the coastal environment off San Diego, California. 2. Petrogenic and biogenic sources of aliphatic hydrocarbons, Environ. Toxicol. Chem., 16: 189–195.

UNEP / IOC / IAEA, 1992. Determination of petroleum hydrocarbons in sediments, Reference Methods for Marine Pollution Studies, 20, UNEP, 75.

UNEP, United Nations Environment Programme 1995. Determination of Petroleum Hydrocarbons in Selected Marine Organisms. Reference Method for Marine Pollution Studies, No. 72, UNEP/IOC/IAEA/FAO.

Volkman, J.K., D.G. Holdsworth, G.P. Neil, B. H.J. Jr., 1992. Identification of natural anthropogenic and petroleum hydrocarbons in aquatic sediments. The Science of the Total Environment, hydrocarbons along the Alexandria Coast. Ves Journees Etud Pollutions, Cagliari C.I.E.S.M.: 257-262.

Wang, Z., M. Fingas, G. Sergy, 1995. Chemical Characterization of Crude Oil Residues from an Arctic Beach by GC/MS and GC / FID. Environ. Sci. Technol., 29 (10): 2622–2631.

Wang, Z., M. Fingas, M. Landriault, L. Sigouin, Y. Feng, J. Mullin, 1997. Using Systematic and comparative analytical data to identify the source of unknown oil on contaminated birds. J. Chromatogram, a 775: 251–265.

Will, G., 1995. Polycyclic aromatic hydrocarbons in water and sediment of the Baltic Sea, Mar. Poll. Bull., 31: 237-248.

Yanan, X., 2010. Thesis submitted for MSc. Characterizations of dissolved organic carbon in prairie surface waters using Fourier transforms infrared spectroscopy, university of Saskatchewan Saskatoon.

Youngblood, W.W., M. Blumer, 1973. Alkanes and alkenes in marine benthic algae. Mar. Biol., 21: 163–172.

Zhengzhen, Z., L. Zhanfei, G. Laodong, 2013. Chemical evolution of Macon does crude oil during laboratory degradation as characterized by fluorescence EEMs and hydrocarbon composition. Marine Pollution Bulletin, 66: 164–175.

Zrafi, I., A. Bakhrouf, M. Rouabhia, M. Saidane, 2013. Aliphatic and aromatic biomarkers for petroleum hydrocarbon monitoring in Khniss Tunisian-Coast, (Mediterranean Sea). Procedia Environmental Sciences, 18: 211 – 220.

Zrafi, N. I., K. G. Zouhour, B. Raouf, C. Imed, R. Mahmoud, S. M. Dalila, 2009. Hydrocarbons in Sea water and interstititial water of Jarzouna - Bizerte Coastal of Tunisia - Mediterranean Sea, Petroleum -31