

## Contamination of Surface Seawaters by Hydrocarbons in the North Western of Suez Gulf

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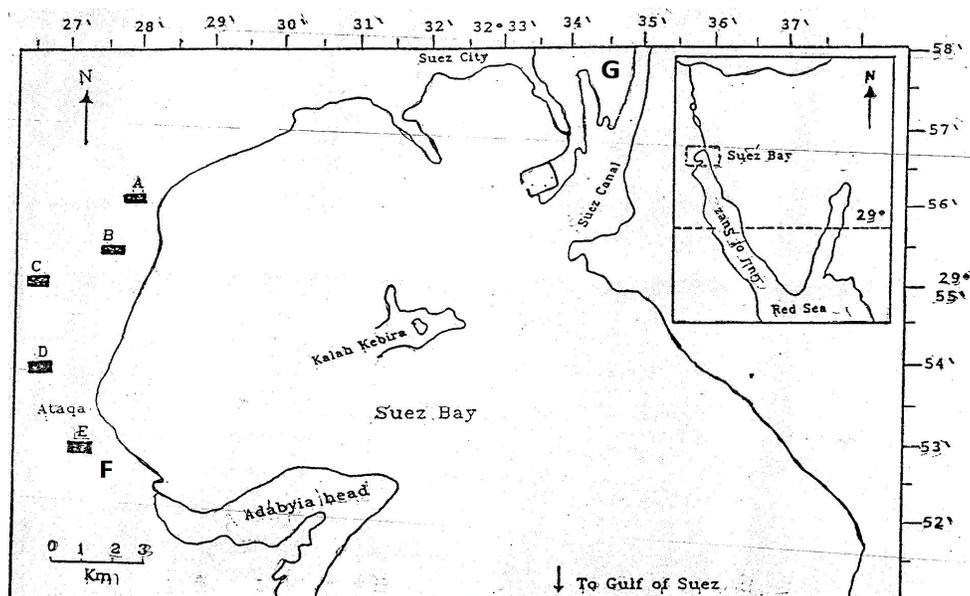
**Summery** The Suez Gulf suffered from extensive chronic petroleum pollution inputs from different sources. So, seven seasonal surface water samples were collected from different locations along the Gulf which extended from inlet of electricity Suez Company to hard steel company, including Attaqa sewage Company during 2011-2012. Each sample was analyzed for hydrocarbons by using gas chromatography, and FT-IR spectrometry to determine the probable source of any petroleum pollutants present. The results show numerous recent inputs of petroleum products especially crude oil at various locations. Dissolved or dispersed petroleum hydrocarbons ranged from 3.89 to 7.46 mg/L and 5.32 up to 37.69 mg/mL for summer and winter water samples respectively, this probably indicates chronic oil pollution. In addition to hydrocarbon concentrations, a number of specific parameters were determined additionally, these include pristane/phytane ratio, carbon preference index of *n*-alkanes, unresolved/resolved compounds ratio, Total hydrocarbon content. Results of gas chromatography analysis indicate that oil pollutants extracted from water samples are at different weathering states. pristane/phytane ratio close to unity and low CPI values < 1 for most of these samples suggest the petrogenic influence. FT-IR spectroscopic analysis reveals considerable amounts of aliphatic and aromatic hydrocarbons in the extracted oil from Suez Gulf. Regular monitoring of aliphatic hydrocarbons contaminant in this region is recommended.

### Introduction

Suez bay is the entrance to red sea is limited by latitudes 29°54 and 29°57 N, and Longitudes 32°28 and 32°34 E. It is an important shipping route for oil tanker and other ships traveling through the Suez Canal, Figure 1. The harbour in the region has always been an important Egyptian gate on the red sea since historical times. Various activities in the harbour lead to an increasing rate of urbanization in the whole region, taking advantage of the site Location. Several

industries have been established all of them along the western coastal stretch of the Suez bay <sup>(1)</sup>. Among vast number of both inorganic and organic pollutants, hydrocarbons are widely occurring contaminants, originating from different sources, material and processes. They play a significant role as they are relatively stable in the natural environment and often accumulate in biological communities and ecosystems and thus, they may represent a human health hazard. Several workers reported that concentrations of dissolved hydrocarbons in seawaters are generally below 10 µg/L in offshore waters and sometimes as light as 40 µg/L in coastal waters <sup>(2)</sup>. Other workers demonstrated that generally very low concentrations of dissolved/dispersed fossil fuel residues in eastern Mediterranean surface waters were being in the range of 10 µg/L to less than 200 µg/L and increases demonstrating that most of the oil pollution is concentrated in coastal waters, sea water samples were collected by some authors <sup>(3)</sup> along Alexandria sea waters and shores in the area extended from Abu-Quir Gulf up to El-A Gamy and Sidi Kirear covering 65kms along the sea shores. Seasonal qualitative and quantitative studies have been made on the contamination of sea waters by oil. Twenty three surface water samples were collected from ten locations of Alexandria sea shores, results of gravimetric analysis show that concentration of oil extracted from winter samples range between 1.875 and 15.857 mg/L. On the contrary, summer water samples show values ranging between 0.616 up to 5.074 mg/L. The concentration of oil content in winter is higher than summer season in the studied location. *n*-alkanes were analyzed by gas chromatography and FT-IR spectroscopy. The Suez Gulf is relatively shallow with a maximum depth of about 64 m, outside its mouth the depth drops sharply to about 1.255 m in contrasts the gulf of Aqaba attains a depth of about 1.355 m and its separated from the deep water of the red sea by an entrance less than 100 m deep. The Suez Gulf has relatively flat bottom with a depth ranging between 55 to 73 m. Hence the Gulf spread shallow basin filled with the surface of the red sea. The Suez Gulf is the most area at risk of pollution in the red sea, particularly oil pollution, it is suffering from extensive chronic petroleum pollution inputs, as coming from

sumed pipelines company terminals, which include both floating and land-based receiving terminals<sup>(1)</sup>. One main source of marine pollution in Suez Canal and Suez Gulf is from ship based sources. Transport of oil continues to play critical role in marine pollution in the northern of Suez Gulf and the Suez Canal. This transportation traffic results in chronic marine pollution discharges of oil ballast water and tank washings by vessels, operational spills from vessels loading or unloading at ports, accident spills from foundered vessels, and leaks from vessels in transit in the Suez bay. Other forms of ship-generated waste include oily sludge, bilges water, garbage and marine debris. The harbors in the region have always been an important Egyptian gate on the red sea since historical times. Various activities in the harbors have lead to an increasing rate of pollution in the whole region. Taking advantage of the site location, several industries have been established all of them along the western coastal stretch of the Suez bay. The studied area extend from inlet of electricity Suez company to the trust Suez company for textile product, Hard steal Suez company and moon beach of Suez Gulf<sup>(4)</sup>.



**Figure 1.** Map of study area and sampling stations

**A:** Inlet of Electricity Suez Company; **B:** Outlet of Electricity Suez Company; **C:** Inlet of Attaqa Sewage Company; **D:** Outlet of Attaqa Sewage Company; **E:** Trust Suez company; **F:** Hard steel Suez Company & **G:** Moon beach.

## Experimental

### Materials and Instrumentation

The reagents were all of analytical reagent grade or chemically pure. All solvents were redistilled and dried before use by standard procedures<sup>(5)</sup>. All the oils-extracted from surface water samples were analyzed according to the standard test method IP318/75<sup>(5)</sup>. Agilent 6890 plus Gas chromatograph with HP-5, 30 m 0.25 mm dim, 0.25  $\mu\text{m}$  film thickness capillary Column. Fourier transforms Infrared spectral analysis (FT-IR) of the prepared oil was measured using ATI Mattson infinity series FT-IR model 960 Moog, USA infrared spectrophotometer was used in the range 4000-400  $\text{cm}^{-1}$ , number of scans 32 with resolution 4.0,<sup>(6)</sup>.

### Methods

#### Area of study on the Suez Gulf

General information about Suez Canal is relatively shallow, the flat bottom with a depth ranging between 55 and 73 m, outside its mouth the depth drops sharply to about 1,255 m. Hence, the Gulf spreads a shallow basin filled with the surface water of the Red Sea. It is the most area at risk of pollution in the Red Sea, particularly oil pollution<sup>(1)</sup>.

#### Samples Collection and Storage

Surface water (0-2 cm) samples were collected from Suez gulf from seven different sites and acidified by HCl as soon as they were collected to adjust brine to  $\text{pH} = 2$ . The studied area lies from Electricity Company to hard and trust company, include Sewage Company and another site is moon beach to determine the hazards of this pollution to human during rest times in beaches. These locations are about 18 km from Suez city Table 1. Along the coast to Attaqa mountain, seven water samples (4 liters each) were taken from onshore sites using pore clean glass as described previously<sup>(6)</sup>. Recovery of oil from sea water is based on the procedure<sup>(7)</sup>.

Site No.	Location	Distance from Suez harbor: (km)	Activities
1	Inlet of Electricity Suez Company	9	Generation of electricity
2	Outlet of Electricity Suez Company.	11	
3	Hard steel Suez Company	18W	Hard steal production.
4	Moon Beach.	18 E	Recreational
5	Inlet of Attaqa Sewage Company	14	Treatment of domestic sewage
6	Outlet of Attaqa Sewage Company	15	
7	Trust Suez company	17	Textile production

**Table 1.** Studied area, their locations, distances from Suez harbor and activities  
**km:** kilometer

### Descriptions of the Locations

Attaqa power station company is located about 9 km from Suez city at Attaqa region and was designed generate electric power, where the natural gas is used as fuel. This location includes sampling from two sites, inlet of power station (1) which is located about 9 km far from Suez city, and (2) outlet of power station which is located about 500 m far from inlet of the station. Hard steel company, site (3) is about 18 km far from Suez city at Attaqa region and designed to produce hard steel and food oil (Afia oil, Rawaby butter) and use water for cooling the product and then drainage at the Gulf and probability to take some waste from products which make pollution in water. Moon beach is located about 18 km east from Suez city and used to make recreation fun for humans and it must be free from all pollutions whether air or water <sup>(1)</sup>. The study on this site is important, in the determination of pollutions caused by loading and unloading of ships and oil spills from the ballast water and industrial waste, which threaten human health. Sewage domestic water is located about 14 km from Suez city at Attaqa region and designed for collection of domestic sewage. This location include sampling from two sites, inlet of plant station site (5) which is located about 14 km far from Suez city,

and outlet of plant station which is located about 1 km from inlet of this station and trust company for textile product site (7) is located about 17 km from Suez city at Attaqa region and designed to production of textile soft or dry good, it take water from Suez bay to liberating free of cotton textiles from sodium hydroxide and the liberated liquid is drained into the Gulf, Figure 1 & Table 1.

#### **Extraction of petroleum oil from surface seawater samples**

100 mL of the 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 unhydrous sodium sulphate (30 g). The extract was then transferred to a weighted beaker and finally evaporated in electrical furnace at 60<sup>0</sup>C till constant weight<sup>(8)</sup>.

The oil content was calculated as:  $\text{mg of oil/L} = \frac{(A-B) \times 1000}{\text{mL of water sample}}$

Where: A & B are the weight of beaker after and before action.

#### **Gas chromatography analysis**

All the oils-extracted from the studied surface water samples were analyzed using capillary column according to the standard test method IP318/75<sup>(5)</sup> for analysis and Testing of petroleum and related products. Agilent 6890 plus, Gas Chromatograph with HP-5, 30 m 0.25m mid, 0.25  $\mu\text{m}$  film thickness capillary column. The Carrier gas was helium at flow rate of 2 mL/min. The injection volume was 0.1  $\mu\text{L}$ . Oven temperature increased from 80<sup>0</sup>C with a rate of 3<sup>0</sup>C/min up to 300<sup>0</sup>C. The injector temperature and detector temperature were 320<sup>0</sup>C.

#### **Liquid column chromatography for separation of (saturates and aromatic and resins components)**

Micro glass columns 10 cm length and 0.8 mm diameter were used to separate saturates and aromatic components. The extracted oil was dissolved in the least amount of n-hexane, and then transferred to the column packed well with alumina. For chromatography (redial) the alumina was activated by heating at 300<sup>0</sup>C for 24 hours (alumina + sample ratio 15: 1). Elution was carried out using n-hexane and then benzene to obtain the saturates and

aromatic fractions respectively, then methylene chloride for resins in each case, elution was continued till the refractive index indicated the pure solvent finally the excess of solvent was evaporated (till constant weight) and the percentage of saturates and aromatics were calculated<sup>(6)</sup>.

#### **Fourier transforms Infrared spectral analysis (FT-IR)**

This technique was used for the characterization of petroleum and its degradation compounds dispersed in samples. The sample was dissolved in carbon tetrachloride (A.R.) and introduced into quartz cell for analysis. ATI Mattson infinity series FT-IR model 960 Moog, USA infrared spectrophotometer was used in the range  $4000-400\text{ Cm}^{-1}$ , number of scans 32 with resolution  $4.0^{(4)}$ .

### **Results and discussion**

#### **Hydrocarbon analysis of surface seawaters pollutant**

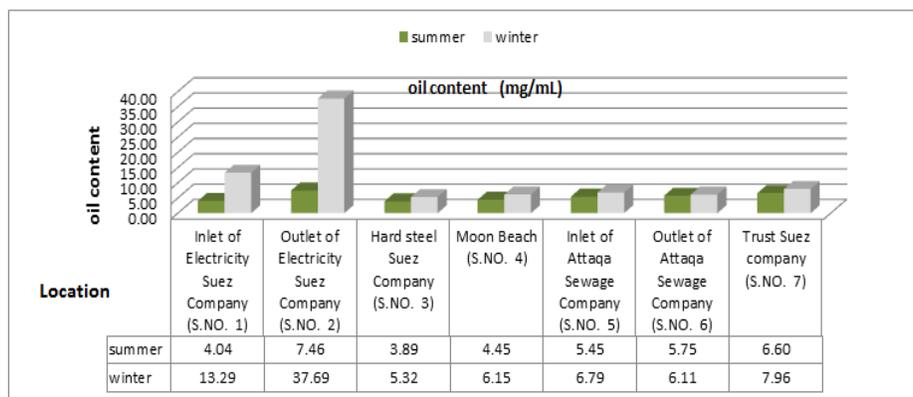
##### **Seasonal variation of oil content (mg/mL) extracted from surface sea waters**

Results obtained from the quantitative determinations of oil content in the studied seasonal water samples Table 2 Fig. 2 ranged from 3.89 to 7.46 mg/L and 5.32 up to 37.69 mg/mL for summer and winter water samples, respectively. The high values were recorded at the outlet of Electricity Suez Company 7.4575 and 37.69 mg/L for summer and winter seasons respectively beside, low value by comparison with the rest samples at the hard steel Suez Company 3.888 and 5.320 mg/L for summer and winter seasons, respectively. Close values were observed between samples 5 (5.45 mg/L) and 6 (5.75 mg/L) for summer and also, between samples 4 (6.15 mg/L) and 6 (6.11 mg/L) for winter water samples respectively. Moreover, the concentration of oil in winter is higher than in summer, this is attributed to the effect of temperature on the oil dissolved or dispersed in the surface waters, weathering process and also, seasonal petroleum activities. The Suez bay area is subjected to pollution from these locations, the amount of wastewater discharged from Attaqa power ( $200\text{ m}^3/\text{hour}$ - $100\text{ m}^3/\text{hour}$ , domestic sewage  $10^3\text{ m}^3/\text{day}$ - cooling water), Attaqa power ( $200\text{ m}^3/\text{hour}$ - $100\text{ m}^3/\text{hour}$ , domestic sewage- $10^3\text{ m}^3/\text{day}$  for cooling water) and Trust company ( $180\text{ m}^3/\text{hour}$  industrial wastewater)<sup>(1)</sup>. All refuses

coming from these sources are discharged directly or indirectly into the Bay. These refuses contain a very large variety of chemicals residues especially, hydrocarbons and poly-aromatic hydrocarbons. Beside, other pollutants from factories outflow, industrial wastes, the shipping inputs from loading and unloading in Suez Gulf, de-ballasting of oil tankers in preparation of loading during off-shore drilling and from coastal refineries and other sources<sup>(9)</sup>. Such undesirable inflows disrupt the ecological balance and affect the quality of water for human use. Hydrocarbon concentration is relatively higher than recommended in the regulations (50 µg/L) of the Egyptian law of Environment of No.4/1994 and International standard values are less than 0.1 mg/mL<sup>(10)</sup>. Results obtained from the present study should be considered when implementing a strategy for the protection and management the Suez Gulf

**Table 2.** Seasonal variation of oil content (mg/mL) extracted from surface sea waters

Site No.	Location	summer (mg/mL)	winter (mg/mL)
1	Inlet of Electricity Suez Company	4.04	13.29
2	Outlet of Electricity Suez Company.	7.46	37.69
3	Hard steel Suez Company	3.89	5.32
4	Moon Beach.	4.45	6.15
5	Inlet of Attaqa Sewage Company	5.45	6.79
6	Outlet of Attaqa Sewage Company	5.75	6.11
7	Trust Suez company	6.60	7.96



**Figure 2.** Histogram representing seasonal variation of oil content (mg/mL) extracted from surface seawaters

### **Comparable of literature data about Petroleum hydrocarbon concentrations in Suez Gulf by various areas in the world**

The results of this study indicate that the total concentration of hydrocarbons which ranged between 3.89 to 7.46 mg/L and 5.32 up to 37.69 mg/mL for summer and winter respectively, higher concentration when comparable to EL-Kuwait country which represents values between (0.0021-0.0036 mg/mL)<sup>(11)</sup>, Oman (0.0013-0.0289 mg/mL)<sup>(12)</sup> and Saudi Arabia, Gulf Coast (0.0002-0.0035 mg/mL)<sup>(13)</sup>, Arabian Sea, Coast Zone (0.0006-0.0188 mg/mL)<sup>(14)</sup>, English Channel (0.0003-0.0014 mg/mL)<sup>(15)</sup>, Saudi Arabia, Red Sea Coast (0.0018-0.0179 mg/mL)<sup>(16)</sup>, Egypt, Red Sea (0.0045 - 0.018 mg/mL)<sup>(17)</sup>, Saudi Arabia Coast, Red Sea (0.0188- 0.412 mg/mL)<sup>(18)</sup>, Arabian Gulf, Saudi Arabia coast, (0.00283-0.0179)<sup>(19)</sup>, Western Coast of the Philippines, Thailand (0.00002-0.015 mg/mL)<sup>(20)</sup>, Saudi Arabia Coast, Red Sea (0.035-0.612 mg/mL)<sup>(21)</sup> and Egypt, Mediterranean Sea which exhibit values ranged between (0.616 - 5.074 mg/mL and 1.875-15.857 mg/mL)<sup>(3)</sup> for summer and winter seasons respectively, but lower values when comparable with those measured in Egypt, Suez Gulf which reverse values ranged between (5639-74800 mg/mL and 1868 - 65698 mg/mL) for summer and winter respectively<sup>(4)</sup>. The samples collected along the Suez Gulf showed much higher levels, indicating that, the historical input from local sources was higher in comparison to the industrial and residential areas. Spatial distributions of dispersed or dissolved oil in samples were significantly different from those in seawater samples, suggesting different sources from aliphatic hydrocarbons. This reflects the influence of discharges from the refinery (oil refinery) and also, of loading and un-loading tanker cargos at the oil terminal. Nevertheless, these data suggest that the level of petroleum hydrocarbons is higher than the level fixed by meteorology and Environmental Protection Administration of Saudi Arabia<sup>(22)</sup>. These areas have the potential to the maritime workshop of the refinery plant. Therefore, these areas have the potential to contaminate the adjacent waters with oil. However, total hydrocarbon concentrations in the

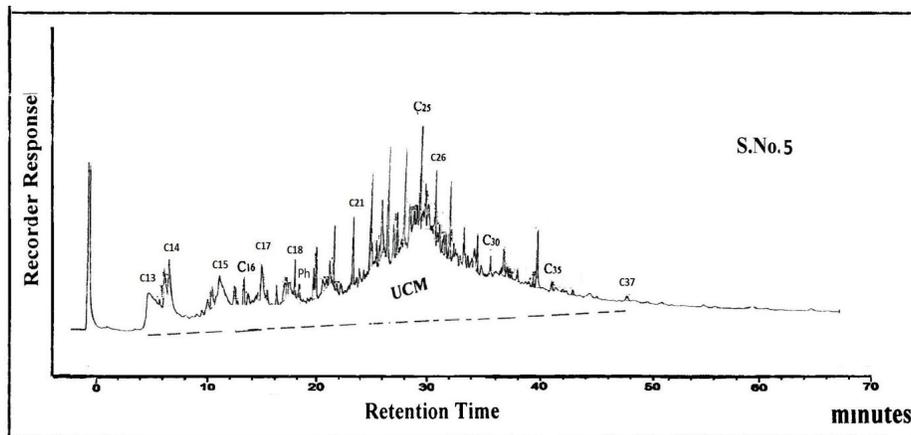
study area were higher than those monitored by several authors in other coastal water, this is due to the Suez Gulf was suffer from extensive chronic petroleum pollution inputs from different sources, as its evident in vicinity sumed pipelines company terminals, which include both floating and land-based receiving terminals. The transportation traffic results in chronic marine pollution discharges of oil ballast water and tank washings by vessels, operational spills from vessels loading or unloading at ports, accident spills from foundered vessels, and leaks from vessels in transit in the Suez bay. It is generally stated that water could be considered polluted when the hydrocarbon concentration is higher than  $2.0 \mu\text{g/L}$  <sup>(23)</sup>. Petroleum products are major pollutants responsible for ecological damage in surface water. The lethal effect of oil concentration occurs in the range ( $1\text{-}10 \mu\text{g/L}$ ), While sub-lethal effect occurs at very low concentrations ( $0.1\text{-}1.0 \mu\text{g/L}$ ). Among the sub-lethal effects of oil contents are extremely toxic to phytoplankton especially in bay area where concentration of both oil phytoplanktons tends to accumulate. Molluscs, crustaceans and fishes are all highly susceptible to oil pollution during their eggs <sup>(24)</sup>.

### **Gas chromatography Analysis**

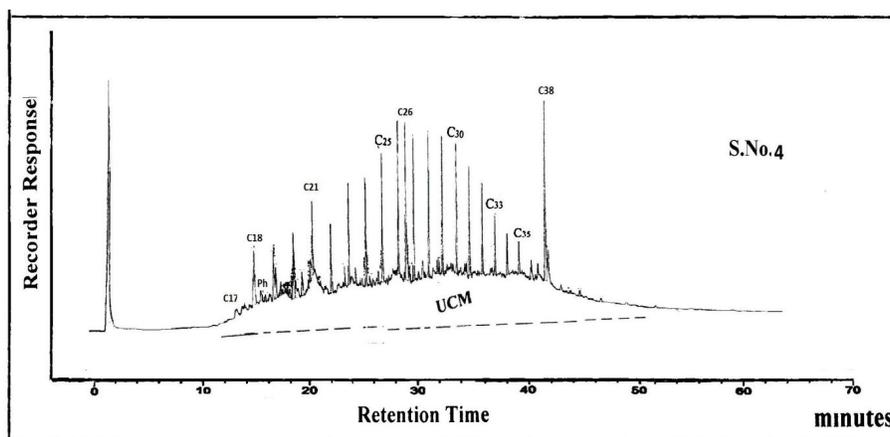
#### **Gas chromatography profiles for oil extracted from seasonal water samples**

The gas chromatograms for the extracted oil from surface water samples are shown in Figures 4 and 5. Studying the general characteristic features of the chromatograms, provide useful information on the origin of pollution and degree of weathering <sup>(25, 26)</sup>. All samples are contaminated by petrogenic origin hydrocarbons regularly spaced over well defined (UCM). The samples were characterized by the presence of a homologous alkane series from  $n\text{C}_{15}$  up to  $n\text{C}_{38}$  with a higher concentration of hydrocarbons in the range  $n\text{C}_{20} - n\text{C}_{38}$  indicating relatively old fractions of oil inputs. Besides, strong odd carbon preference index at  $n\text{C}_{25}$ ,  $n\text{C}_{27}$  and  $n\text{C}_{29}$  in addition to a relatively high UCM envelop. The paraffinic hydrocarbons decreased regularly to different extents indicating various degree of weathering. The predominating peaks  $n\text{C}_{25}$  and  $n\text{C}_{23}$  are found in all samples revealing an additional biogenic origin introduced

from phytoplankton, zooplankton and benthic algae<sup>(27, 28)</sup>. The presence of two UCM in the majority of the samples indicating that pollutants originate either from region was subjected to more than one spill and or mixed crude oils.



**Figure 4.** Gas Chromatograms for oils extracted from summer sample no. 5 as example of GC analysis



**Figure 5.** Gas Chromatograms for oils extracted from winter sample No. 4 as example of GC analysis

### GC parameters

#### Parameters that distinguish between biogenic and petrogenic origin

The carbon preference index (CPI), CPI data of seawater samples ranged from 0.924 to 2.020 for summer season, also winter waters samples show values ranged between 0.840 and 2.252 Table 3, which reveal a mixed biogenic and petrogenic contamination origin. But the assumption cannot be accepted by discussing the profiles of the chromatograms obtained which are shown to be

typically petrogenic. On the other hand, petroleum oils are characterized by CPI values around 1.0<sup>(29)</sup>, the presences of high concentrations of *n*-paraffin *n*C<sub>25</sub> cause this confusion given an indication of the biogenic origin. The CPI values were calculated again without taking in consideration the value of *n*C<sub>25</sub> peak areas. Table 3; show the results for the CPI correct values are ranged from 0.82 to 1.77 for summer and 0.715 up to 2.136 in winter seasons. These indicate that the petrogenic origin is mainly predominating while little biogenic contaminations can be detected especially that of *n*C<sub>25</sub>.

**Pristane / phytane ratio**, biogenic hydrocarbons are characterized by more abundant pristane than phytane, suggesting a photo plankton input which result in an abnormally high pristane / phytane ratio <sup>(30)</sup>. summer and winter water samples exhibit no values due to extensive and sever weathering effects on the low molecular weight *n*-alkanes range from <*n*C<sub>20</sub>. Table 3, shows values 0.014 and 0.374 for site (5) in both summer and winter seasons, predicting mainly a petrogenic contamination, the ratio Pr/Ph <1 confirming a petrogenic contamination <sup>(31, 32)</sup>.

***n*C<sub>10</sub> – *n*C<sub>25</sub>/*n*C<sub>17</sub> – *n*C<sub>25</sub> ratio**, this ratio is used to indicate the addition of algal biosynthesized hydrocarbons and or degree of weathering<sup>(3)</sup>. Data obtained from studied seasonal water samples show that most of samples exhibited close values between 1.0 to 1.017. This means no significant variations in the degree of weathering. On the other hand, the rest of samples Table 3 had slightly higher values ranged from 1.022 up to 1.484 and 1.097 up to 1.156 for summer and winter seasons respectively, being exposed to less weathering effect.

**Unresolved complexes mixture (UCM)**, in addition to the chromatographically, resolved compounds and unresolved complex mixture (UCM) of hydrocarbons is present in most samples, it is appears in the range of *n*C<sub>13</sub>-*n*C<sub>37</sub> Figures 4 and 5. However, in some samples it appear as a bimodal hump in the range of *n*C<sub>17</sub> to *n*C<sub>25</sub> and *n*C<sub>29</sub> to *n*C<sub>35</sub>. The UCM is generally considered as a mixture of many structurally complex isomers and homologous of branched and cyclic hydrocarbons that can't be resolved by capillary

columns<sup>(33)</sup>. Further, the presence of UCM in the aliphatic fraction is considered as the most important indicator of petrogenic pollution by weathered or degraded petroleum residues, when the maximum height occurs mainly in the higher molecular weight. Yet, it has also been linked to bacterial degradation of natural organic inputs algal detritus<sup>(34)</sup>. The UCM % concentration varies from 22.324 up to 117.015 mg/mL and 82.059 to 97.054 mg/mL for summer and winter season respectively, Table 3.

**Unresolved/resolved complex mixture ratio (U/R)**, the ratio of unresolved compounds to the resolved U/R ones is used for prediction of the origin of pollutants, where a value  $>4$  predict a petrogenic origin of pollutant, while value  $<4$  will show a biogenic origin of pollution<sup>(35)</sup>. The value U/R in Table 3, ranged from 0.921 to 1.567 and 0.415 up to 8.326 for summer and winter respectively, which confirm the petrogenic origin mixed with biogenic origin<sup>(32)</sup>, finally the highest value due to high concentration of aromatic and naphthenic compounds.

#### **Parameters detecting vaporization and dissolution**

Evaporation is the single most important and dominant weathering process, in particular for the light petroleum products, in the short term after spill. The loss can be up 70% and 40% of the light volume of light crude and petroleum products in the first few days following spill<sup>(37)</sup>. The rate of which oil evaporates depends primarily on the oil composition. The more volatile components on oil or fuel contains the greater extend and rate of its evaporation. Table 4 for seasonal samples show close values between sites (1, 7, 4, 6) have values of 0.920, 0.941, 0.950 and 0.999 respectively for  $> nC_{17} / Tn.$  alkanes ratio in summer water samples, also close values between winter samples (1, 2, 4 and 7) have 1.0 value, for  $> nC_{17} / Tn.$  alkanes ratio. The ratio  $\leq nC_{17} / Tn.$  alkanes represented values between 0.051 and 1.559 for summer water samples and 0.020 up to 0.132 for winter water samples. Moreover, weathering ratio ( $WR = \text{sum } nC_{23} - nC_{34} / \text{sum } nC_{11} - nC_{22}$ ) which varies from

**Table 3.** Seasonal variation for prediction of biogenic and petrogenic contamination for surface Seawater samples

Parameter S.NO.	summer						winter					
	CPI	CPI*	Pr/Ph	$nC_{10}\text{-}nC_{25}/$ $nC_{17}\text{-}nC_{25}$	UCM%	U/R	CPI	CPI*	Pr./Ph.	$nC_{10}\text{-}nC_{25}/$ $nC_{17}\text{-}nC_{25}$	UCM%	U/R
1	2.02	1.769	n.d.	1.017	45.425	1.156	2.252	2.136	n.d.	1.000	97.054	0.415
2	1.23	1.010	n.d.	1.000	22.324	0.987	1.242	1.044	n.d.	1.000	89.28	8.326
3	0.94	0.820	n.d.	1.022	103.007	1.038	1.040	0.995	n.d.	1.000	82.058	0.545
4	n.d.	n.d.	n.d.	1.000	88.690	0.921	0.841	0.715	n.d.	1.000	85.23	0.990
5	0.93	0.850	0.014	1.484	117.145	1.567	0.971	0.828	0.374	1.156	80.55	4.142
6	1.12	0.990	n.d.	1.000	78.151	0.983	1.763	1.752	n.d.	1.097	88.91	8.011
7	1.71	1.540	n.d.	1.000	55.586	0.977	1.138	0.932	n.d.	1.000	87.990	7.330

**n.d.:** under the limit of detection; **CPI\*:** CPI value without the ( $n\text{-}C_{25}$  or  $n\text{-}C_{23}$ ) peak value; **Pr/Ph:** pristane (Pr) over phytane(**Ph**) ratio;  **$nC_{10}\text{-}nC_{25}/ nC_{17}\text{-}nC_{25}$ :** normal alkanes from  $nC_{10}\text{-}nC_{25}$  over normal alkanes from  $nC_{17}\text{-}nC_{25}$ ; **UCM:** Unresolved complex mixture; **Pr/Ph:** ~ 1 petroleum contamination, >1 Biogenic contamination<sup>(29)</sup>, **CPI:** ~ 1 petroleum contamination, >1 Biogenic contamination<sup>(35)</sup>; **U/R:** >petroleum contamination, <4 Biogenic contamination<sup>(4 and 35)</sup>;  **$nC_{10}\text{-}nC_{25}/ nC_{17}\text{-}nC_{25}$ :** <2 petroleum contamination, >2 Biogenic contamination<sup>(36)</sup>.

samples (1, 2, 4 and 7) have 1.0 value, for  $>nC17/ Tn.alkanes$  ratio. The ratio  $\leq nC17 /Tn. alkanes$  represented values between 0.051 and 1.559 for summer water samples and 0.020 up to 0.132 for winter water samples. Moreover, weathering ratio (WR=  $\text{sum } nC_{23} - nC_{34} / \text{sum } nC_{11} - nC_{22}$ ) which varies from 0.906 to 6.217 and 1.067 up to 5.843 for each summer and winter water samples. These variations indicate various petroleum inputs at different times (Someone and some old one). In addition, the high values indicate high weathering; this can be confirmed by observing the low concentrations of low molecular weight *n*-hydrocarbons Table 4 and Figures 4 and 5, shows the lowest values being highly weathered, as a result of long exposure to photo oxidation, vaporization, dissolution and biodegradation.

**Table 4.** GC Parameters for variation of vaporization and dissolution in surface seawater samples

Parameters S.NO.	summer			winter		
	$>nC17/$ <i>Tn.alkanes</i>	$\leq nC17/$ <i>Tn.alkanes</i>	WR	$>nC17/$ <i>Tn.alkanes</i>	$\leq nC17/$ <i>Tn.alkanes</i>	WR
1	0.920	0.083	1.895	1.000	n.d.	n.d.
2	1.000	n.d.	5.400	1.000	n.d.	3.960
3	0.860	0.150	0.910	0.981	0.020	2.751
4	0.950	0.051	2.340	1.000	n.d.	n.d.
5	0.730	0.250	1.150	0.870	0.132	1.246
6	0.999	1.559	6.127	0.898	0.102	1.067
7	0.940	0.060	2.880	1.000	n.d.	5.850

$>nC17/ \text{ total } n\text{-alkanes}$ : normal alkanes $> nC17/ \text{ total normal alkanes}$ ;  $\leq nC17/ Tn.alkanes$ : normal alkanes $<nC17/ \text{ total normal alkanes}$ ; **WR**: weathering ratio =  $(\text{sum } nC_{23} - nC_{34} / \text{sum } nC_{11} - nC_{22})$  (4&27).

### Parameters detecting the degree of Bio-degradation

Biodegradation of hydrocarbons by natural of micro organisms (such as many species of bacteria, fungi, and yeasts), represents one of the primary mechanisms by which petroleum and other hydrocarbons pollutants are eliminated from the environment (38). The biodegradation of petroleum and other hydrocarbons in the environment is a long term complex process whose quantitative and qualitative aspects depend on the type, nature and amount of the oil or hydrocarbons present, the ambient and seasonal environment,

conditions (such as a temperature, oxygen, nutrients, water activity, salinity, pH, and the composition of autochthonous microbial community). Hydrocarbons differ in their susceptibility microbial attack. The biodegradation effects straight chain *n*-alkanes more than branched alkanes, and alkanes more than the other hydrocarbons classes and both pristane and phytane (isoprenoids) having branched structure are relatively more resistant to biodegradation than the *n*- alkanes<sup>(39)</sup>.

***n*C17/ Pristane, pristane** (Pr) and phytane (Ph) are the most common isoprenoid detect in Suez Gulf. Seasonal surface seawater represented disappearing of both pristane and phytane as a result of severe weathering on the low molecular weight alkanes, except for inlet of Attaqa sewage company site no. (5), summer and winter seawaters show values 0.984 and 1.32 respectively in Table 5, also outlet of Attaqa sewage company reverse value 0.995. Generally, rates of biodegradation weathering increase by decreasing the values<sup>(40)</sup>.

***n*C18 / Phytane**, the values obtained in Table 5 for summer and winter samples show close values between summer waters samples. Close values between samples 1(0.238) and 5(0.218) respectively, also moon beach display value 3.088 in summer and Inlet of Attaqa Sewage Company exhibits value 0.032 in winter, generally lowest values shown high biodegradation<sup>(41)</sup>.

***Tn*-alkanes / Pristane**, inlet of Attaqa sewage company recorded high value 26.994 at the summer season indeed, each of inlet and outlet Attaqa sewage company winter samples recorded values 21.500 and 18.280 respectively, as shown in Table 5 which may be reflect either the difference in the weathering degrees due to the different exposure times to the environmental conditions or due to the different origins from which the pollutants had been derived<sup>(42)</sup>.

***Tn*- alkanes /Phytane**, the ratios of summer water samples vary as shown in Table 5 between 4(95.392) and 5(10.093) respectively, indicates different rates of biodegradation, weathering which increase by decreasing the values. This rate in the following sequences:  $5 < 1 < 7 < 4$ . On the other hand, winter season samples not determined as result of disappear once of phytane (Ph), which due

to the extensive weathering on the low molecular weight alkanes in the range less than  $nC_{20}$ .

**$nC_{14}$ -  $nC_{18}$  / five isoprenoid in between ratio**, the ratio of  $n$ -alkanes /Isoprenoids is defined as the ratio of the sum of  $nC_{14}$ -  $nC_{18}$  over the sum of farnesane, trimethyl  $C_{13}$ , norpristane, pristane and phytane<sup>(43and 44)</sup>, this ratio is often used to indicate the degree of biodegradation, weathering, because  $n$ -alkanes are readily degraded than the branched species<sup>(4)</sup>. Both seasonal studied water samples show values ranged between (0.170 – 3.260) and (0.008– 7.910) for summer and winter seawaters respectively, Table 5.

**T $n$ -alkanes /Tiso- alkanes**, normal alkanes are usually degraded more rapidly than the isoprenoid alkanes, so this ratio is used as an index for the degree of weathering (mainly biodegradation). This ratio is decrease with weathering effect<sup>(45)</sup>. Table 5 show the following sequences respectively for increasing biodegradation, weathering  $1<3<7<5<6<4<2$  and  $5< 6< 2< 1<3<7$  for both summer and winter water samples respectively. The relatively higher differences between these two sequences and that of the other parameters are due to the differences in the added biogenic hydrocarbons specially that of  $nC_{25}$ .

### Hydrocarbon group's analysis

Through weathering dramatic changes in the composition and toxicity of petroleum products occurs. A Knowledge concerning the hydrocarbon types of oil pollutants is necessary especially as the saturate fraction is severely affected weathering<sup>(46and3)</sup>. While, the aromatic hydrocarbon especially the more condensed molecules are not metabolized or weathered to the same degree. A high value for saturates content can be used to detect pollutants derived from un-weathered or slightly weathered tank washing. Saturates/aromatic ratio may indicate the relative weathering degree. Three water samples were chosen for this study in Table 6 which denotes that these oils have variable values for both saturates and aromatic contents beside, Sat/Aro., ranged from 0.828 to 1.573. The relatively higher value for samples 2(1.573) and 3(1.099) presumably

points out that saturates hydrocarbons for both samples have not been exposed to long weathering time relative to other sample.

### **FT-IR Spectral analysis**

FT-IR Spectra for oil extracted from Suez Gulf water samples are shown in Figure 6. The characteristic band for aliphatic hydrocarbons appear as a strong bands at  $2922$  and  $2857\text{ cm}^{-1}$  due to stretching vibration of methylene groups (vas  $\text{CH}_2$ ) and (vs  $\text{CH}_2$ ) stretching vibration respectively <sup>(3)</sup>. Strong bands at wave number  $2923\text{ cm}^{-1}$  and  $1461\text{ cm}^{-1}$  represent  $-\text{CH}_2$  stretching and  $-\text{CH}_2$  bending frequencies and peak at  $730\text{ cm}^{-1}$  for aliphatic crude oil has a paraffinic nature <sup>(4, 44)</sup>., these data indicates that oil has a paraffinic nature. In addition, to a strong band at  $1374\text{ cm}^{-1}$  for waters samples 1, 2 & 3 in summer and winter seasons respectively. Moreover, a medium band appears at  $810\text{ cm}^{-1}$  for summer water sample significant for naphthenic compounds. Also, medium band at  $740\text{ cm}^{-1}$  due to out of plane bending of - C-H group in mono and polynuclear aromatic hydrocarbons <sup>(47)</sup>, Tri-substituted alkanes from  $800\text{-}840\text{ cm}^{-1}$  as a strong to medium bands. A strong band of mono-substituted benzene at  $700\text{-}750\text{ cm}^{-1}$  and strong band at  $1729\text{ cm}^{-1}$  duo to carboxylic easter<sup>(48)</sup>.

**Table 5.** Seasonal effects of weathering biodegradation on surface seawater samples

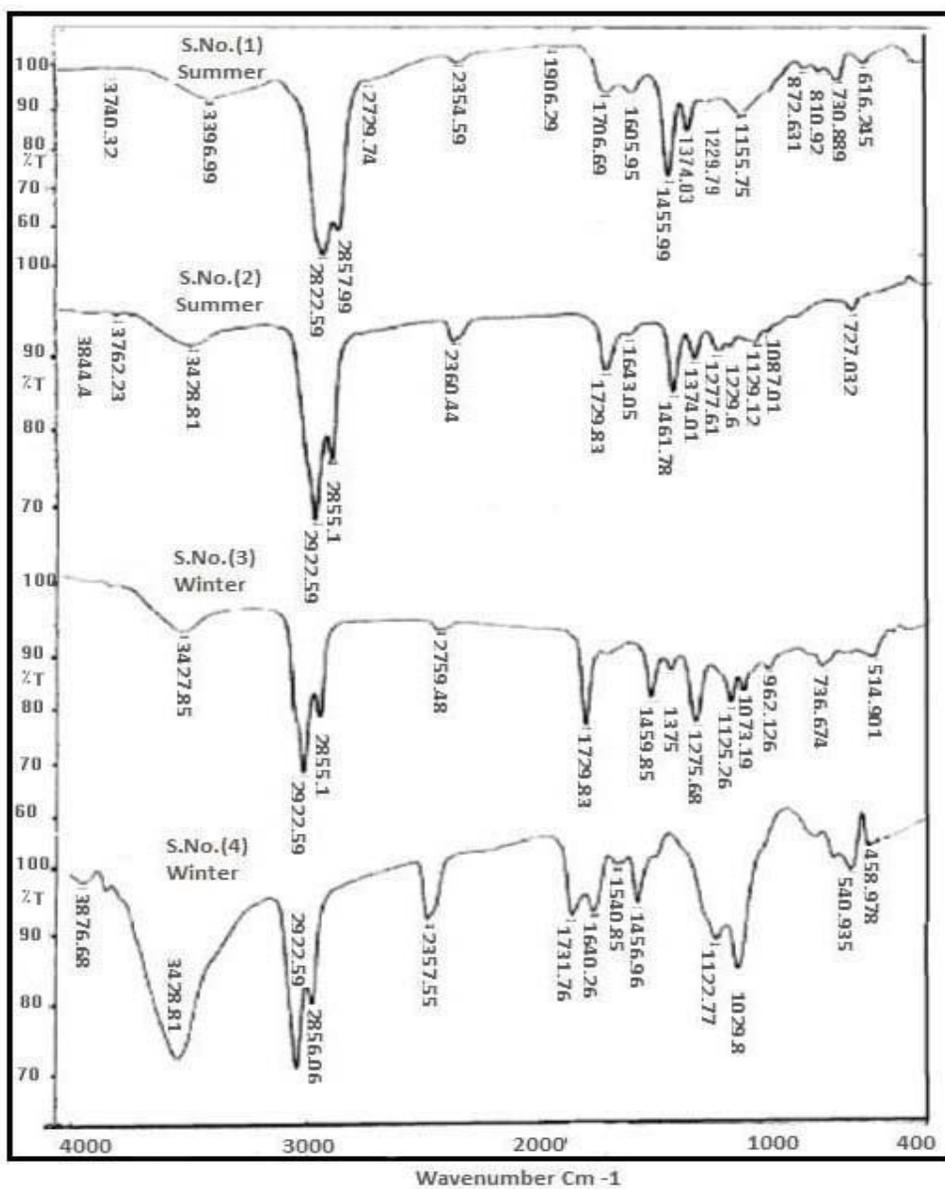
Parameters S.NO.	summer						winter					
	$nC_{17}$ /Pr.	$nC_{18}$ /Ph.	Tn alk./Pr.	Tn alk./Ph.	$nC_{14-}$ $nC_{18}$ / Five iso	Tn. alk./iso- alk .	$nC_{17}$ / Pr	$nC_{18}$ /Ph.	Tn alk./Pr.	Tn alk./Ph.	$nC_{14-}$ $nC_{18}$ / Five iso	Tn. alk./iso- alk.
1	n.d.	0.238	n.d.	16.600	1.000	0.060	n.d.	n.d.	n.d.	n.d.	0.008	0.720
2	n.d.	n.d.	n.d.	n.d.	n.d.	4.030	n.d.	n.d.	n.d.	n.d.	n.d.	0.470
3	n.d.	n.d.	n.d.	n.d.	n.d.	0.600	n.d.	n.d.	n.d.	n.d.	4.118	1.880
4	n.d.	3.088	n.d.	95.400	n.d.	2.960	n.d.	n.d.	n.d.	n.d.	7.910	n.d.
5	0.984	0.218	26.994	10.094	0.170	0.975	1.32	0.038	21.500	0.310	1.070	0.150
6	n.d.	n.d.	n.d.	n.d.	3.260	1.260	0.995	n.d.	18.280	n.d.	0.0105	0.293
7	n.d.	n.d.	n.d.	20.750	n.d.	3.260	n.d.	n.d.	n.d.	n.d.	0.395	8.200

$nC_{17}/Pr.$ : normal alkanes of  $nC_{17}$  over pristine;  $nC_{18}/Ph.$ : normal alkanes of  $nC_{18}$  over phytane, **Pr/Ph**: pristane (Pr) over phytane (**Ph**) ratio; Total normal alkanes/ phytane;  $nC_{14-}nC_{18}$  / **Five iso.** : Normal alkanes from  $nC_{14}$  to  $nC_{18}$  over five isoprenoids in between; **Tn.alk.** / **Tiso.alk.**: Total normal alkanes /Total iso alkanes <sup>(4)</sup>.

**Table 6.** Hydrocarbon group's analysis of some selected water samples.

S. No.	Location	Sat. % wt	Aro. % wt	Resin % wt	Sat./Aro. ratio
2	Outlet of Electricity Suez Company	47.771	30.365	21.864	1.573
3	Hard steel Suez Company	35.429	32.224	32.347	1.099
5	Inlet of Attaqa Sewage Company	37.302	45.063	17.635	0.828

**Sat:** Saturate; **Aro:** Aromatic

**Figure 6.** FT-IR absorption spectra for some selected seasonal water samples

### Conclusion and Recommendations

This work aim to monitoring and assessments the contamination which discharged into Suez Gulf, the main activities that may cause pollution are loading and unloading of ships in harbor, Industrial activities, sewage, ballast water petrochemical industrial and different industrial chemical plants, navigation and recreation activities. Dissolved and dispersed petroleum hydrocarbons in Suez Gulf ranged from 3.888 to 7.46 mg/mL and between 5.32 up to 37.69 mg/ mL for summer and winter respectively, which confirmed high levels of contamination by hydrocarbons on the studied location, (International standard values are less than 0.1 mg/mL) . GC analysis for oils extracted from surface water indicates that such hydrocarbons are mainly of petroleum origin in both dissolved and dispersed states; however some extracted oils have a mixed biogenic petrogenic nature. It can also be, concluded from GC parameters that oils are of different weathering rates which denotes continuous oil inputs from different sources. In spite of chronic petroleum pollution, the predominance of  $nC_{25}$ ,  $nC_{27}$  and  $nC_{29}$  alkanes could be used as biological markers in polluted waters. All sites were exposed to hydrocarbons pollution with different rates whereby the sites near to the petroleum activities are much more affected than the touristic sites. FT-IR spectroscopic analysis indicates high concentration of both aliphatic and aromatic hydrocarbons in addition to naphthenic compounds. Because the Suez Gulf is used in many areas as a recipient of waste water from different sources this; study recommended that pollution control for wastewaters disposing into it should be improved. More detailed studies are required to assess the effects in Suez Gulf water from different sources of pollution and monitoring should be conducted at least twice per year. This; study recommended that pollution control for wastewater disposing into it should be improved by separation of oils water Alsabourh before dumping into the Gulf. Follow the accumulation of contaminants in the water and beaches to take the necessary precautions to reduce it, development of a system for rapid intervention in the event of oil disasters, serious

commitment to application of environment law to the age of 1994 for the protection of water and beaches.

### References

- 1- Remip working Groups (WG2), State of oil pollution and Management in Suez Gulf Region, Revised July 23, P (15), (2008).
- 2- M. Erhardt, J. Klungsor, and G. Patrick, Marine Pollution Bulletin, 20(11) 560-565, (1989).
- 3- A. R. Mousa, N. A. Farid, M. M. Soliman and O. E. Ahmed, 15<sup>th</sup> international conference on petroleum, Mineral Resources and development, 8-10, April, Egyptian Petroleum Research Institute, Cairo, Egypt (2012).
- 4- M. K., Eman, Thesis submitted for MSC, Al-Azhar University, (2013).
- 5- IP standards, for analysis and testing of petroleum and related products, Institute of petroleum, London, V1, 1993,
- 6- A R. Mousa, N. A. Farid, M. M. Soliman and Omayma E. Ahmed, Egypt J. petrol., 10 No. 2, pp. 1-14 (2000).
- 7- R. Ravid, O.H. Oren, H. Harnung, Marine Pollution Bulletin 16(2), 81-84 (1985).
- 8- E. A. Omayma, Ph.D., Faculty of science institute of environmental studies and research Ain shams university p.163, (2005).
- 9- C. Wood and Mc Garty, Report and Recommendations, Report for MCS, 58, pp. (2003a).
- 10- M. M. Soliman, O. E. Ahmed, N. A. Farid, and A. R. Mousa, Egypt J. petrol., 8 (1), 77-85, (1999).
- 11- M.I. El-Samra, H. I. Emara, and F. Shunbo, Marine Pollution Bulletin, Vol. 17, No. 2, pp. 65-68 (1986).
- 12- M.I. Badawy, I. S. AL-Mujaing, M. d. Hernandez, Mar. Poll., 26, 457-460, (1993).
- 13- M.G. Ehrhardt, K.A. Burns, Marine Pollution Bulletin, 27,187-197, (1993).
- 14- R. Sen-Gupta, S. Z. Qasim, S. P Fondekar, and R.S. Topgi, Mar. Pollut., Bull.11, 65-68, (1980).
- 15- T.W. Fileman, and R. J. Law, Mar. Pollut. Bull., 19, 390-393, (1989).

- 16- S. S. Lihaibi, and S. T. AL-Ghamdy, Mar. Sci., vol. 8, pp. 83-89, 17- S.M. Shereet, Emirates Journal for Engineering Research, 14 (1), 65-71, (2009).
- 18- H. AWAD, Proceedings of the First Conference on Environmental Sciences, Sabha, Lybia, 27-31 January, 1990.
- 19- M. C. Bicego, E. Z. Lamardo, R. R. Weber, Occanogr, 51(unico):33-38 (2003).
- 20- S. Saramun, and G. Wattayakorn, Southeast Asian Fisheries Development Center, (1998).
- 21- H. Awad, Bulletin of the National Institute of Oceanography & Fisheries, Egypt, 14, (1), 293-296, (1988).
- 22- MEPA, Environmental protection standard Document, No.1409- 01. Meteorology and Environment protection Administration, Saudi Arabia, P17, (1982).
- 23- P.D. Keizer, and D.C. Gordon, J. Fish. Res. Bd, Can, 30, 1039-1045, (1973).
- 24- B. H. Hanan, Ph. D. Thesis entitled Fac. Sci., Al-Azhar University, (2007).
- 25- M. Watanabe, S. Tanabe, R. Tatsukawa, M. Amano, N. Miyazaki, E.A. Petrov and S.I. Khuraskin, Archives of Environmental contamination and toxicology, 37, 396 – 407, (1999).
- 26- J.k. Volkman, S. M. Barrett, and G.A. Dunston, Organic Geochemistry 21, 407 – 413, (1994).
- 27- M.I. Roushdy, M. Brakat, and O. Eman, The 15<sup>th</sup> International Conference on Petroleum, Mineral Resources and Development 8-10- April, Cairo, Egypt, (2012).
- 28 - H.T. Al. Saad, W.A. Farid, and A.Y. Al-Adhub, Mar .Sci, 2011, 26(2), 182-196, (2012).
- 29- P.M. Medeiros, M.C. Bicego, Marine Pollution Bulletin 49, 461 – 769, (2004).
- 30- M. Stenhauer, E. Crecelins, and W. Steinhauar, Marine environs –Res, 37(2) 129-163, (1994).
- 31- M.S. Steinhaver, and P.D. Boehm, marine environmental research, Vol.33, No 4, pp. 223-253, (1992).

- 32- B. Saida, k. Soumaya, B. Ioanna, S. Alain, and Er. R. Hassan, *International Journal of Geosciences*, 2011, 2, 562-572 (2011).
- 33- J. I. Bouloubassi, Fillaux, A. Saliot, *Marine Pollution Bulletin*, vol. 42 no. 12, pp.1335-1346, (2001).
- 34- M.A. Gaugh, S. J. Rowland, *nature*, Vol. 344, No. 12, PP. 648-650, (1990).
- 35- I. Tolosa, S. Mora, M. Sheikh, J. Oieslami, M. Villeneuve, J. Bar tocci, and C. Abd Cattini, *Marine pollution Bulletin*, 48 (1-2), 44-60, (2004).
- 36- J. Paynet, J. R. Clayton, and J. Ph. Charles, *Oil Petrochemical pollution*, V2, No.3, P173, (1985).
- 37- T.k. Dutta, and S. Harayama, *Technology*, 34, 1505, (2000).
- 38- R. C. Prince, *Crit Rev. Mirobia*, 119,217 – 242, (1993).
- 39- C. F. Guor, W. Yah-shem, C. Cheng-Nan, and T. Stung, *TTO, Chemosphere*, 64, 1242, (2006).
- 40- Z. Wang, M. Fingas, and G. Zhem, *Chromatographic analysis of the environment*, 1026-1096, (2003-b).
- 41- X. C. Wang, R. F. Chen, and A. Barry, *Estuarine, Coastal and shelf science*, 58,917-928, (2003a).
- 42-M.K. Nagla, Thesis submitted for Ph. D., Azhar University, P83-85, (2006).
- 43-R. I. A. dullah, N. M. Khalil, and M. I. Roushdy, the 17<sup>th</sup> International Conference on Petroleum Mineral Resources and Development, Feb., 9 – 11, (2014).
- 44- O. E. Ahmed, N. A. Ali, S. A. Mahmoud, and M. M. Doheim, *International Journal of Modern Organic Chemistry*, Florida, USA, 3(1), 1-17, (2014,).
- 45- D. Munoz, M. Guiliano, P. Doumenq, F. Jacquot, P. Scherrer, and C. Mille, *Mar. Pollut. Bull.*, 34, 868, (1997).
- 46- M. Aceves, J.O. Grinalt, J. Albuiges, F. Broto, L. Comllas, and M.J. Gassrot *Chromatography*, V436, P503-509, (1998).
- 47- N. Aske, H. Kallevik, J. Sjoblom, *Energy Fuels*, 15 (5), PP. 1304-1312, (2001).
- 48- S.A., Sayed, A.S., El. Sayed, A.M. Zayed, *Journal of Applied Science and Environmental Management*, vol. 8. No. 1, PP 71-79, June, (2004).