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ARTICLE

Seasonal Effect on Biomarkers of Exposure to Petroleum Hydrocarbons in the Coasts of North Western Suez Gulf, Egypt

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ABSTRACT

Petroleum hydrocarbons of surface water were collected from eight locations of from the coasts of north western Suez Gulf, Egypt. The extracted petroleum hydrocarbons were determined by gas chromatography–flame ionization detector and quantified by integrating the areas of both the resolved and unresolved components. The results confirm that the concentration is relatively higher than the recommended in the regulations of the Egyptian low of Environment of No.4/1994 of petroleum products. At various locations, The dissolved petroleum hydrocarbons ranged from 5.639 to 74.8 and 1.868 to 65.698 mg/ml for summer and winter seasons, respectively. This indicates that chronic oil pollution, in addition to hydrocarbon concentrations, the diagnostic indices used shows that the hydrocarbons in the area were comes from biogenic, petrogenic and anthropogenic sources. FT-IR spectrometric analysis confirms the petrogenic nature of pollutants.

1. Introduction

The Suez Canal is located in the northeast of Egypt (Figure 1) extended from port Tewfik in South with overall length 162 kms and 22.5 m water depth, the Suez Canal passes through an area of considerable agricultural, industrial and tourist activity. So the relation between human activities and environmental changes in Suez Canal require knowledge of trends in water quality and understanding of the management of aquatic habitats. This is related to sewage and/or industrial waste discharges along the western coast of the Bay. The pollutant varies from raw sewage, oil spills, and industrial effluents to garbage which has tremendous impacts on the marine environment [1]. The marine environment of the bays in Suez Gulf is subjected to mixed sources of pollution (industrial, agricultural and domestic sewage) through the direct discharge of El-Kabanon drain, which is considered as the main industrial and sanitary drain. Research was carried out on heavy metal pollution in the region, where the bay is subjected to industrial run-off from oil refineries, fertilizer plants, and power station in addition to sewage and garbage [2]. Various physical and chemical properties that influence

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the survival of aquatic organisms in water and sediment include but not limited to the following; temperature, pH, conductivity, dissolved oxygen, salinity, turbidity, chlorophyll, total suspended solids, total dissolved solids, sediment moisture, organic carbon and matter [3]. These qualities are highly instrumental to the assessment of the level of damage done to the waterways and their deviation from natural levels can result in ecosystem deterioration [4]. Inflow of municipal effluents, storm waters and industrial discharges into the rivers, lakes, estuary, bay and oceans as a result of global increase in urbanization and industrialization are channels for serious environmental pollution with relatively high consequences on human health, aquatic ecosystem balance, as well as social and economic development [5]. The monitoring them in water resources is highly paramount for the protection of human and aquatic lives [6]. The aims of this study are therefore to investigate the pollution status of Suez Gulf determining the physicochemical properties of the water, concentrations of the aliphatic and total petroleum hydrocarbons in both the water and also to identify the possible sources of contaminants using various ratios and indexes on the *n* - alkanes.

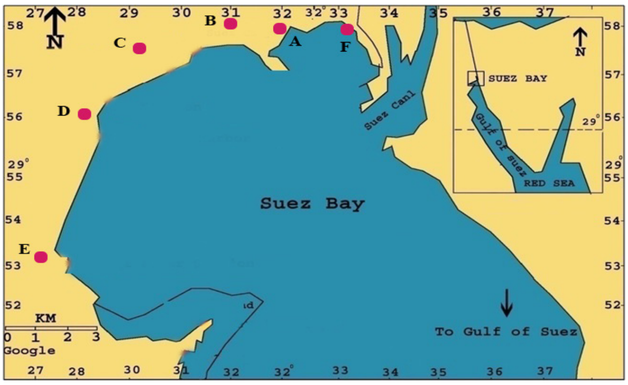

Figure 1. Map of Suez Bay showing position sources of pollution.

Notes: A: Al-Nasr oil Company; B&C: inlet and outlet of Suez oil company; D: Outlet of Electrical station company; E: Fertilizer Factory & F: AL-Osra & Al-Melaha beaches.

2. Materials and Methods

2.1. Chemicals and Sample Collection

Surface water (0-2 cm) samples were collected from Suez Gulf. The area under consideration includes industrial zones and beaches. Table 1 shows locations which extend from Suez Harbor to Fertilizer factory and from Al-Osra to Al-Melaha beaches along Suez Gulf with a maximum distances about 21 km along Suez Gulf. Each location has an area of 1x3m.

2.2. Physico- Chemical Properties:

Multi - parameter probe was used for the in situ measurement of pH values, Electrical conductivity, salinity, total dissolved salts (T.D.S), total solid salts (T.S.S), total salts (T.S), dissolved oxygen (D.O.), biological oxygen demand (BOD), carbon oxygen demand (COD), chloride ion (Cl^-), sulphate ion (SO_4^{-2}), nitrates (NO^-_3), phosphates (PO^{-3}_4) and total alkalinity for the Seawater.

Table 1. Studied sites, their locations, activities and distances from Suez harbor

Site No.	Locations	Activities for each site	Distance from Suez Harb. (Km)
1	Suez Harbor.	Loading and discharge, marine transportation, including tanker operations	2(Km)
2	Al-Nasr oil Company	petroleum refinery of the crude oil	5(Km)
3	Inlet of Suez oil company	petroleum refinery of the crude oil	7(Km)
4	Outlet of Suez oil company.	petroleum refinery of the crude oil	9(Km)
5	Outlet of Electrical station company.	Industrial treatment- Unit for domestic sewage treatment	10(Km)
6	Fertilizer Factory	Unit for domestic sewage treatment	18(Km)
7	Al-Osra beach	Oil residue and solid wastes	20(Km)
8	Al-Melaha beach	Oil residue and solid wastes	21(Km)

2.3. Extraction of Petroleum Oil

100 ml of the seawater sample was shaken with 100ml of carbon tetrachloride in a separating funnel for 15 minutes. 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 [7]. The oil content was calculated using the following equation:

mg of oil/l = (A-B) x1000 / ml of water sample

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

2.4. 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[7]. Agilent 6890 plus, Gas chromatograph attached to computerized system with chemstation software condition of operation [8] column: HP-5,30m0.25m mid, 0.25 µm film thickness. Carrier gas: Helium at flow rat of 2ml/min, injection: Split (1:30) 0.1 µI, oven temperature: Initial temperature 80◦C 3◦C/min up to 300 ◦C. The injector temperature 320 ◦C and detector temperature: 320 ◦C.

2.5. Fourier Transforms Infrared Spectral Analysis (FT-IR)

The samples 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 nm, number of scans 32 with resolution 4.0 [9].

3. Results and Discussion

3.1. Physicochemical Properties

The physicochemical properties of water samples are summarized in Table 2. The pH of most natural waters is in the range of 6.0–8.5. The higher pH values could be obtained from eutrophic and salty water while lower values are usually from dilute water containing high levels of organic materials [10, 11]. *PH values:* ranged from 7.23 up to 8.20 in summer and 7.33 to 8.30 in winter with average values 7.62 and 7.65 respectively (Table 2). Normal pH value in seawater is between 8.0-8.2 at the surface, decreasing to 7.7-7.8 with increasing depths [11]. In the Suez Gulf, pH values were found to increase southwards, where the maximum pH of 8.20 & 8.30 was recorded at Inlet and outlet of Suez Oil Company for summer and winter, respectively while, a minimum pH values was recorded at Al-Osra beach and Suez Harbor for summer and winter respectively. The pH values are affected by the disposal of mainly acidic sewage and industrial effluents as well as the oil refineries effluents distributed in the Suez Bay. In general pH of Suez Gulf is slightly alkaline vary from region to another depending upon the location of sampling and independent on the season.

The highest values of alkalinity in outlet of Suez Oil Company in winter, the lowest values of alkalinity in Fertilizer factor in summer (Table 2).

Table 3 shows that values of suspended solids (SS) is higher in the outflow effluent than those in the inflow water and also, the values in winter is higher, 46851 mg/L ,than the values in summer (36502 mg/l). This is due to the presence of the oil globules and the discharge of huge amounts of suspended solids from the dew-axing and coke distillation department as well as hydrodesulphurization unit into the drain.

TDS includes inorganic salts as calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulphates besides small amount of organic matter that are dissolved in water. Table 3~~:~~ Shows that the highest values of TDS at Suez Harbor attained in summer. TDS values ranged between 34965 mg/L to 36330 mg/L in summer and 34860 mg/L to 36260 mg/L in winter with average values 356447.7 mg/L and 35525 mg/L, respectively. TDS values increase than the maximum permissible limit according to the low 4\94 that TDS 2000 mg/L.

The content of dissolved oxygen (DO), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) is ranged from 2.13 to 3.97 mg~~O_2~~ /L in summer and 1.49-2.24 mg~~O_2~~/L in winter (Table 3). This decrease in the content of dissolved oxygen may be due to the presence of mercaptans compounds in the oil participate in consuming the dissolved oxygen or due to the presence of layer of oil on the surface of the water in the outlet effluent which prevent the oxygen to be dissolved. The content

Table 2. PH, EC and Salinity values for the surface seawater samples from Suez Gulf.
E.C: **µ**s/cm, Alkalinity: mg (CaCO3/L), *Alkalinity*, (mg ($CaCO_3$/L)

Season		Summer				Winter			
S.No	**Location**	**PH**	**E.C µs/cm**	**Salinity**	**Alkalinity (mg) ($CaCO_3$/L)**	**PH**	**E.C µs/cm**	**Salinity**	**Alkalinity (mg)($CaCO_3$/L)**
1	**Suez Harbor.**	7.45	51.90	33.9	110	7.33	51.60	33.4	135
2	**Al-Nasr oil Company**	7.38	51.59	33.9	120	7.58	51.80	33.6	145
3	**Inlet of Suez oil company**	8.20	49.95	56.1	140	8.0	49.80	51.4	150
4	**Outlet of Suez oil company.**	8.03	50.80	54.3	180	8.30	50.50	51.6	200
5	**Outlet of Electrical station company.**	7.80	50.42	32.7	90	7.88	50.10	32.4	150
6	**Fertilizer Factory**	7.50	51.60	51.8	80	7.42	51.50	51.5	115
7	**Al-Osra beach**	7.23	50.70	32.9	145	7.35	50.60	32.8	170
8	**Al-Melaha beach**	7.40	50.40	50.6	160	7.35	50.10	50.1	185
Range		7.23-8.20	49.95-51.90	32.7-56.1	80-180	7.33-8.30	49.80-51.80	32.4-51.6	115-200
Average		7.62	50.92	43.27	128.12	7.65	50.75	42.1	156.25

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Table 3. Seasonal variation of T.S, T.D.S &T.S.S: mg\L, BOD and COD (mg / L).

S.No.	Location \ Season	Summer						Winter					
		T.S mg\l	T.D.S mg\l	T.S.S mg/l	DO mgO$_2$/l	BOD mgO$_2$/l	COD mgO$_2$/l	T.S mg\l	T.D.S mg\l	T.S.S mg/l	DO mgO$_2$/l	BOD mgO$_2$/l	COD mgO$_2$/l
1	Suez Harbor.	38904	36330	11021	3.42	270	36.8	48058	36120	12038	2.24	140	128
2	Al-Nasr oil Company	38300	36113	15219	2.98	232	276	48002	36260	17042	2.13	144	296
3	Inlet of Suez oil company	36432	34965	1466	2.46	172	202.4	46542	34860	16641	1.92	86	264
4	Outlet of Suez oil company.	38024	35566	15054	3.97	272	231.2	44675	35350	16036	2.13	146	240
5	Outlet of Electrical station company.	37040	35294	16640	2.13	362	55.2	47196	35070	16726	2.02	180	160
6	Fertilizer Factory	32709	36120	17728	3.55	242	92	46102	36050	20052	1.77	212	160
7	Al-Osra beach	34890	35490	11238	2.20	240	66	47830	35420	12018	1.49	120	128
8	Al-Melaha beach	35721	35280	17675	2.23	210	94	46404	35070	23334	1.81	180	150
Range		32709-38904	34965-36330	1466-17728	2.13-3.97	172-362	36.8-276	44675-48058	34860-36260	12018-23334	1.49-2.24	86-212	128-296
Average		36502	35644	13255	2.867	250	131.7	46851	35525	35610	1.938	151	190.7

Note: NT.S, T.D.S &T.S.S: mg\L,BOD & COD (mg / l).

of BOD and COD in the outlet effluent exceeded than the recorded values in the inflow water (Table 3).

The increment of BOD and COD is mainly attributed to the increase in the total petroleum hydrocarbons and mercaptans compounds in the drain, or may reflect the importance of active mixing and gas exchange in this area [11]. Furthermore, the presence of high amount of organic compounds in the effluents could enhance the growth of microorganisms in wastewater [12]. Comparing the obtained results of BOD (Table 3) with the tolerable level for pure water, higher level was particularly reported at the northern part of the Gulf, indicating the presence of detectable load of domestic wastes discharging into this region.

Table 4 shows the decrease of nitrite values in the inflow water this may be due to the reduction of nitrite to ammonia by the action of bacteria [1] or may be due to the oxidation of it to nitrate. On the other hand, the presence of petroleum compounds increases the values of nitrite as confirmed in Table 4. Al-Nasr oil company and Fertilizer Factory have highest values of 0.188 and 0.180 ppm for summer and winter seasons, respectively. Nitrate considered as the final stage in the oxidation of nitrogen compounds and measure the quantity of organic matter. Seasonal variation of nitrate (Table 4) indicates that nitrate ranged between 0.01 ppm and 8.02 ppm in summer with average value of 2.39 ppm, while the concentration in winter ranged from zero ppm to 7.65ppm with average value of 2.15 ppm.As shown from the achieved results, the nitrate content decreased during winter for both inflow and outflow effluent this may be attributed to its uptake by microorganisms and phytoplankton while the increase during summer could be attributed to the nitrification of ammonia to nitrite and nitrate produced by the biochemical decomposition of dead planktons. The nitrate values were found to be low in two seasons and within the permissible maximum limits of 40 ppm. Table 4 shows the average values of phosphate concentrations in summer is 0.034 mg/L and 0.020 mg/L in winter. The highest concentration of orthophosphate and total phosphate are found to be higher in summer due to the decay of planktons which contain phosphate in its body [11]. The comparison study of the present data of nutrients with the previous records in the Suez Gulf and other regions indicates that they are equivalent to other reports (Table 5). At the area of study, the concentrations of nitrite, nitrate and phosphate were 0.0-0.188, 0.01-8.02 and 15-61ug/L, respectively. The high concentrations are indicators for the presence of pollutants of high activity viz. sewage discharge, industrial effluents and oil refineries concentrated at the northern part of the Gulf (Suez Bay). It is also evident that the area of investigation can be divided into two regions; Suez Bay region as an eutrophic Water (high productivity) and the part of the Gulf as going southward to Safaga which is considered as oligotrophic water (low productivity). The mean concentrations of sulphate are shown in Table 4 . The increase of sulphate values may be due to the petroleum wastes containing sulphure which ranged from 0.1 to 3.4% (by weight) where sulphure compounds detected as sulphate, sulphid and mercaptans. The reduction of sulphate in petroleum wastes depends on several factors necessary to sustain the life of bacteria; the most important of these are the concentration of sulphate, organic matter, and

Table 4. Seasonal variation of nitrite, nitrate, phosphate, sulphate, chloride and fluoride.

S.No	Location \ Season	Summer						Winter					
		Nitrite ppm	**Nitrate ppm**	**Phos. mg\l**	**Sulph ppm.**	**Chlor. mg\l**	**Flou. ppm**	**nitrite ppm**	**nitrate ppm**	**Phos. mg\l**	**Sulph ppm.**	**Chlor. mg\l**	**Flou. ppm**
1	**Suez Harbor.**	0.0	6.98	0.037	55.6	366.79	0.27	0.0	6.0	0.025	55.0	362.54	0.24
2	**Al-Nasr oil Company**	0.188	1.31	0.057	127.03	288.21	0.075	0.165	1.00	0.047	129.00	386.79	0.007
3	**Inlet of Suez oil company**	0.183	8.02	0.020	982.79	559.63	1.13	0.180	7.65	0.015	987.02	554.01	1.11
4	**Outlet of Suez oil company.**	0.185	1.17	0.015	265.74	100.57	0.054	0.175	1.10	0.011	264.70	98.68	0.052
5	**Outlet of Electrical station company.**	0.0	0.19	0.028	638.002	289.72	0.045	0.0	0.10	0.020	638.00	280.71	0.040
6	**Fertilizer Factory**	0.184	1.45	0.027	148.2	270.43	0.060	0.180	1.40	0.013	145.02	265.24	0.050
7	**Al-Osra beach**	0.0	0.01	0.061	20.0	264.82	0.024	0.0	0.0	0.012	20.0	264.00	0.022
8	**Al-Melaha beach**	0.0	0.01	0.028	18.6	265.33	0.020	0.0	0.0	0.022	16.4	260.30	0.020
Range		0.0-0.188	0.01-8.02	0.015-0.061	18.6-982.79	100.57-559.63	0.020-1.13	0.0-0.180	0.0-7.65	0.011-0.047	16.4-987.02	98.68-386.79	0.007-1.11
Average		0.0925	2.39	0.034	282.99	300.68	0.209	0.0875	2.15	0.020	281.89	309.03	0.192

Note: Nitrite (ppm), Nitrate (ppm), phosphate(mg\L), sulphate (ppm),chloride (mg\L)and fluoride(ppm)

Table 5. Nutrient salts concentrations (ug/L) of seawater in the present study compared with other region

Area \ Parameter	NH_3-N	NO_2-N	NO_3-N	PO_4-P	References
Gulf of Suez	0.18- 4.14	0.07- 0.45	0.48- 4.6	0.8-1.04	[26]
AL Khor, Suez	3.54	0.38	2.06	0.62	[27]
Gulf of Suez	1.54	0.20	0.52	0.47	[28]
Suez Canal	2.44	0.59	2.03	0.81	[28]
Suez Bay	3.25	0.49	1.48	0.85	[29]
Suez Bay	8.86	0.33	3.42	0.45	[30]
Jeddah	-----	0.28	9.69	-----	[26]
Dongonab Bay	-----	-----	4.9-7.2	0.3-1.5	[31]
Abu Qir Bay	1.23	0.07	0.88	0.58	[32]
Eastern harbor of Alexandria	3.16	0.95	6.79	0.56	[33]
EL Max Bay	20.38	o.48	1.87	1.62	[34]
Suez Gulf	-------	------	0.17	------	[24]
Suez Gulf	------	0.0-0.188	0.01-8.02	15-61	This work
Oligotrophic level **Eutrophic level**	0.5 2.02	---- ----	0.5 4.0	0.05 ----	[35, 36]

both of nutrient and dissolved oxygen [13]. The data recorded in Table 4 display the highest values of 982.79 and 987.02 ppm of sulphate at Inlet of Suez Oil Company For summer and winter, respectively. Chloride~~s~~ concentrations recorded in Table 4 showed that values in summer higher than in winter. The values in summer ranged between 100.57 to 559.63 mg/L with average value~~s~~ of 300.68 mg/L, while in winter values ranged between 98.68 to 386.79 mg/L with average 309.03mg/L. Flouride are present as fluorspar in rocks (limestone, sandstone) and as cryolite in igneous rocks (granite) [14] The seasonal variation in fluoride concentration show highest values of 1.13 and 1.11 ppm at Inlet of Suez Oil Company in summer and winter seasons respectively. This is due to the decay of living organisms and the presence of the crust earth, rocks and ground water containing fluoride during the drilling.

3.2. Seasonal Concentration of Oil Content

Results obtained for the quantitative determinations of oil

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content in the seasonal study for the water samples (Figure2). Close values were observed between Suez Harbor and El-Melaha beach have rates of 6.222 to 6.543 mg/ml, respectively. The winter season samples also represented close values between Suez harbor , El-Nasr oil company and Suez fertilizer company have values of 5.25, 5.37 and 5.04 mg/ml, respectively. On the other hand, oil content concentration ranged between 1.868 to 65.69 mg/ml for winter samples. The main source for hydrocarbon contamination of El-Suez harbor is mainly by ballast water from oil tankers crossing all the studied locations beside sewages effluents and drains. Generally, concentration of oil content are highly in summer than winter season could be attributed to some petroleum related activities present.

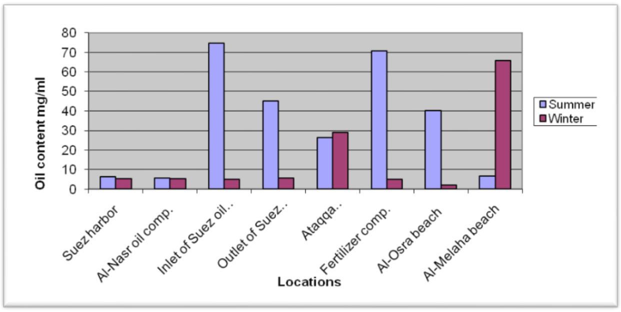

Figure 2. Histogram representing seasonal concentration (mg/ml) of oil content extracted from surface water samples

3.2.1. GC–for Oil Extracted from Seasonal Water Samples

Summer and winter Seasonal studied samples show chromatogram similar to those for petroleum weathered profiles which consist of a number of peaks over a wide number of n- alkenes range starting from nC_{14} up to nC_{40} (Figures 3, 4). These Figures show an example of GC analysis for selected samples. The ontained chromatograms show that compounds lighter than $n\text{-}C_{11}$ lost during the evaporation and extraction. These *n*–paraffin's are standing out at equal distance above well defined un-resolved compounds (UCM). The presence of two UCM in the majority of the samples indicate that the pollutants originate either from mixed crude oils and or the region was subjected to more than one spill which gave the primary feature of the GC chromatogram. The resulted patterns for the locations are the bimodal *n*-alkane distribution diagnostics of tanker ballast washing and Biogenic sources for hydrocarbons are indicated by the dominance of the odd *n*-alkanes (nC_{17}, nC_{19}, nC_{25}, nC_{29}) which are synthesized by marine algae and higher terrestrial plant. The paraffinic hydrocarbons are shown to be decrease regularly to different extents indicating various degree of weathering waxes [15].

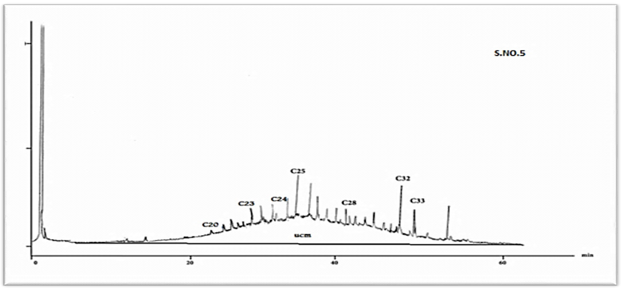

Figure 3. Gas Chromatograms of extracted oil from summer water samples no. 1 as example of GC analysis

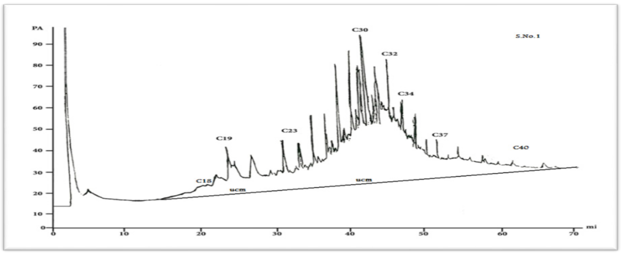

Figure 4. Gas Chromatograms of extracted oil from winter water samples no. 5 as example of GC analysis.

3.2.2. Parameter Detecting Vaporization and Dissolution

In the short term after a spill, evaporation is the single most important and dominate weathering process, in particular for the light petroleum products. The loss can be up 70% and 40% of the volume of light crude and petroleum products, in the first few days following a spil. The rate at which oil evaporates depends primarily on the oil composition. The more volatile components in oil or fuel contains the greater the extend and rate of its evaporations.

(1) $\leq nC_{14}/T.n.alkanes$ *ratio*, data obtained and presented in Table 6 show values ranged between 0.128 to 0.817 for winter samples; whereas, in summer the values is not detected in most samples except for the outlet of Suez oil company is 0.042. The low values probably due to the loss of a major part of low molecular weight paraffin's by dissolution, evaporation and or photo-Oxidation [2].

(2) $\leq n\ C_{17}/T.\ n.\ alkane$, data obtained for this ratio Table 6 exhibit variable values ≤ 1 indicating severe weathering process through evaporation and or photo-Oxidation, dissolution and biodegradation. The oil in the marine greatly affect by different environmental factors [16]. Seasonal summer samples exhibit values between 0.017 to 0.351 while, in winter the values ranged between 0.054 to 1.00 which considered to be less weathered than summer samples.

(3) $n.\ alkane > n\ C_{17}$, the n.alkanes range > n C17 is

relatively more resistant to different weathering processes than lower n-alkanes [17]. Seasonal samples (Table 6) as expected shows higher values ranging between 45.64 to 88.79 for summer samples and 0.546 to 41.22 for winter due to the loss of low molecular weight alkanes in the first part.

(4) *nC_{14}- n C_{18}/ Isoprenoids* [18], the ratio of n –alkanes / Isoprenoids is defined as the ratio of the sum of n C_{14}- n C_{18} over the sum of farnesane , trimethyl C_{13}, norpristane, pristine and phytane, [17]. Table 6 show that summer samples have high values ranged from 0.378 to 14.468 indicates that they were freshly spilled in these sites and accordingly less weathered oils, while winter exhibited low values from 0.097 to 4.196.This is due to intensive weathering on the studied stations.

(5) *nC_{12}–nC_{25}/nC_{17}-nC_{25},* the ratio is used to indicate the addition of algal biosynthesized and/or degree of weathering [19]. Data obtained for summer and winter season samples (Table (6) exhibited close values ranged between (1.000- 1.024) and (1.000-1.078), respectively. This means no seasonal significant variations in degree of weathering and indicates petrogenic origin. On the contrary, the rest of samples had slightly higher values ranging from 1.045 to 2.073 and 1.350 to 4.283 for summer and winter samples, respectively. This is due to being exposed to less weathering degree and reveal biogenic origin.

(7) *Weathering ratio*, the weathering ratio WR = (n C_{23}-nC_{34}) / (n C_{11}-n C_{22}) [11] which varies from 1.175 to 9.195 for summer sample~~.~~ while, winter samples show values between 0.0562 to 4.724 indicates high weathering effect (Table 6). This can be confirmed by the presence of low concentrations of low molecular weight~~,~~ hydrocarbon.

3.2.3. Biodegradation

(1) *nC_{17}/ pristane ratio*, the ratio nC_{17}/pr and nC_{18} /ph usually used as indicators ~~of~~ for hydrocarbons revealed for most samples and degraded material of biogenic inputs [11]. However, most samples show high values of nC_{17}/pr ratio which could be related to the relatively high contents of nC_{17} in several stations. Most of summer and winter water samples (Table 7) exhibit~~s~~ very high weathering effect on the n-alkanes <n C_{20} which lead to the absence of niether pristane nor phytane ratios. Generally nC_{17}/pr ratio considered as an additional index of contamination which showed less values of 0.901 for El-Nasr oil company indicates high weathered effect, whereas each of outlet of Suez oil company and El-Melaha beach display higher values of 10.519 and 4.884, for summer samples, respectively. On other hand, El-Osra and El-Melaha beaches exhibit values 0.714 and 0.896 but, Outlet of Suez company and El-Nasr oil company have 4.312 and 12.192 values for winter samples indicates the biogenic addition. The rates of biodegradation weathering ~~i~~ increases by decreasing the values, the rate are in the following sequences: Summer water site 4 < site 8 <site 2 winter site 2 < site 4 < site 8 and site 7.

(2) *n-C_{18} /phytane ratio*, the obtained data Table 7 show values ranged between 0.397 to 20.3455 for summer samples whereas, winter samples exhibit values ranged

Table 6. GC Parameter for seasonal vaporization and dissolution of water samples

Season	**Summer**								**Winter**							
S.NO	**Range of *n*-alkane**	**Oil content mg/L**	**<C14/ T.n alk.**	**<C17/ T.*n* alk.**	**>C17**	**C_{14}-C_{18}/ Isoprenoids**	**$nC_{12}nC_{25}$ /$nC_{17}nC_{25}$**	**WR**	**Range of *n*-alkane**	**Oil content mg/L**	**<C_{14}/ T.n alk.**	**<C_{17}/ T.*n* alk**	**>C_{17}**	**C_{14}-C_{18}/ Isoprenoids**	**nC_{12}-nC_{25}/ nC_{17}-nC_{25}**	**WR**
1	**C_{18}-C_{40}**	6.222	N.D	N.D	75.88	N.D	1.000	4.471	C11-C24	5.250	0.128	0.128	39.11	0.097	1.078	0.056
2	**C_{15}-C_{38}**	5.638	N.D	0.0226	74.14	0.378	1.009	8.081	C11-C19	5.366	0.246	0.222	21.27	0.662	1.350	N.D
3	**C_{18}-C_{37}**	74.8	N.D	1.0	40.21	7.900	1.000	5.394	C17-C34	4.878	N.D	0.053	41.22	4.196	1.0	1.294
4	**C_{14}-C_{37}**	45.027	0.0416	0.3512	45.64	14.468	2.073	1.175	C11-C18	5.677	0.153	0.450	21.27	3.317	1.197	N.D
5	**C_{16}-C_{33}**	26.262	N.D	0.0478	62.50	1.445	1.045	1.430	C20-C33	28.972	N.D	N.D	30.53	N.D	N.D	4.723
6	**C_{15}-C_{36}**	70.888	N.D	0.0517	88.79	N.D	1.024	2.464	C11-C18	5.040	0.508	0.936	1.109	1.249	2.838	N.D
7	**C_{17}-C_{35}**	40.297	N.D	0.0464	61.74	N.D	1.000	9.195	C11-C18	1.868	0.418	0.973	0.546	0.667	4.914	N.D
8	**C_{16}-C_{40}**	6.5428	N.D	0.0170	82.79	2.308	1.019	4.399	C11-C17	65.698	0.817	1.000	N.D	0.895	4.283	N.D

Note: N.D: not determine

between 0.279 up to 26.353 which are significant for petrogenic inputs and these values are consistent with the fact that phytane cannot occur biogenic ally [8]. The rate of biodegradation weathering for each of summer and winter samples are: Summer samples site 2 <site 5 <site 8 site 4, winter site 1 <site 4 < site 3 and site 6.

(3) *Total n-alkanes/pristane*, Table 7 shows great variation of the detected values (387.97) for site 8 and (52.505) for site 2, summer samples. In addition, (4.037) site 7 and (43.801) site 2, in winter samples may reflect the difference in the weathering degree due to different exposure times to the environmental conditions or due to the different origins from which the pollutants had been derived. Also, the lowest values for summer and winter samples shows the highest weathering degree and has the sequences: Summer samples site 8 <site 4 < site 2, winter site 2 <site 4 < site 8 and site 7.

(4) *Total n –alkanes /phytane*, the observed ratios are listed in Table7. It is clear that there are a variation between values of different sites as; 59.737 for site 4 and 1213.55 for site 2 in summer, whereas 4.402 for site 6 and 180.5 site for winter samples, according to following sequences: Summer samples site 2 <site 5 < site 8 <site 4, and winter site 1 <site 3 < site 4 < site 6.

(5) *Total n–alkanes /Total Iso-alkanes*, normal alkanes are usually degraded more rapidly than isoprenoid alkanes, so this ratio is used as an index for the degree of weathering (mainly biodegradation). The ratio decreases with weathering [7]. Summer samples (Table 7) show close values between sites 1 (3.147), site 2 (3.142), site 5(1.910) and site 7 (1.837), whereas winter samples exhibit close values between site 2 (0.770), site 3 (0.772), site 6 (0.212), site 7 (0.26). The results obtained show the following sequences for increasing biodegradation weathering, for seasoal samples, Summer samples site 6 <site 8 < site 1 <site 2 <site 4 <site 5 < site 7 <site 3. The winter samples Site 1 <site 2 < site 1 <site 3 <site 4 <site 5 < site 7 <site 6 <site 8. The relatively higher differences between this sequences and that of the other parameters is due to the differences in the added biogenic hydrocarbons especially that of n-C_{25}.

3.2.4. Distinguish between Biogenic and Petrogenic Origin

(1) *Pristane /Phytane ratio*, it is clear that the ratio ~1.0 [20], predicating mainly a petrogenic contamination. Table 8 show low values for sites 4, 8 in summer and site 4 in winter samples as pristane /phytane ratio is not detected for the rest samples due to extensive weathering on the studied location. On the contrary, El-Nasr oil company exhibit high value 2.397, it must be noted that the station is dominated by algae which are responsible for biosynthesis of pristine suffer from different degree of biodegradation and indicat a biogenic contamination.

(2) *Carbon preference Index (CPI)*, biogenic hydrocarbons are characterized by a distribution pattern of n-alkanes showing odd carbon numbered alkanes being much more abundant than even carbon numbered alkanes mainly in the range of (n-C_{21} to n-C_{33}). This indicates high CPI values, which is defined as the sum of the odd carbon numbered alkanes to the sum of even carbon numbered

Table 7. Seasonal effect of weathering "Biodegradation" on surface water samples

Season / S.NO.	Summer					Winter				
	nC_{17}/ **pr**	***n***C_{18}/ **ph**	***n*.alk /pr**	***n*.alk./ph**	***n*.alk/ iso.alk**	***n***C_{17}/**pr**	***n***C_{18}/**ph**	***n*.alk/pr**	***n*.alk./ph**	***n*.alk/ iso.alk**
1	N.D	N.D	N.D	N.D	3.147	N.D	26.353	N.D	186.5	0.814
2	0.901	20.355	52.505	1213.55	3.142	12.192	N.D	43.801	N.D	0.770
3	N.D	N.D	N.D	N.D	0.468	N.D	1.605	N.D	48.218	0.771
4	10.519	0.397	125.079	59.737	2.373	4.342	7.615	16.969	13.870	0.632
5	N.D	6.140	N.D	108.70	1.911	N.D	N.D	N.D	N.D	0.439
6	N.D	N.D	N.D	N.D	14.78	N.D	0.279	N.D	4.402	0.212
7	N.D	N.D	N.D	N.D	1.837	0.714	N.D	4.034	N.D	0.261
8	4.884	1.6423	387.97	60.202	5.341	0.896	N.D	5.479	N.D	0.108

Note: N.D: not determine

Table 8. Seasonal prediction of biogenic and petrogenic contamination for surface water samples.

Season	Summer					Winter				
S.NO	**Pr/ph**	**CPI**	**CPI***	**U/R**	**UCM%**	**Pr/ph**	**CPI**	**CPI***	**U/R**	**UCM%**
1	N.D	1.043	0.912	4.670	82.30	N.D	0.104	0.104	1.559	30.31
2	2.311	2.659	2.396	1.780	64.07	N.D	6.091	6.091	0.714	74.88
3	N.D	1.230	1.010	0.431	61.88	N.D	0.515	0.479	0.452	35.33
4	0.477	0.906	0.773	5.880	86.32	0.8173	0.602	0.602	1.170	60.89
5	N.D	1.044	0.863	12.67	92.68	N.D	1.021	0.795	1.642	51.0
6	N.D	0.696	0.546	19.91	95.21	N.D	1.176	1.176	1.081	52.50
7	N.D	8.565	3.718	2.470	71.20	N.D	1.366	1.366	0.438	40.34
8	0.155	0.498	0.428	0.975	49.37	N.D	1.196	1.196	0.991	70.35

Note: N.D: not determine

alkanes. On the other hand, petroleum oils are characterized by CPI values around 1.0 [20]. Thus CPI data from summer samples ranged from 0.498 to 8.565; , whereas winter samples represented values between 0.104 to 6.091 as shown in Table 8. But this assumption cannot be accepted by discussing the profiles of the chromatograms obtained which are shown to be typically petrogenic origins [14]. Thus the CPI values were calculated again without taking in consideration the value of (n-C_{25}) peak areas. The results show that the CPI corrected values are ranging from 0.428 to 3.718. This indicates that petrogenic origin is mainly predominating, while little biogenic contaminations can be detected especially that of (n-C_{25}), for summer samples. Table 8 also, show that CPI correct values for sites 3, 5 are 0.480 and 0.795 respectively, while the rest samples have CPI corrected values not differ from the CPI values this due to weathering effect on the range ≥24 n-alkanes , on winter season samples.

(3) *Un-resolved complex mixture (UCM)*, un-resolved complex mixture (UCM)hump is a measure of the extend of weathering .The values of UCM percent (Table 8) reveals that all samples are highly sensitive to weather for summer and winter seasons which indicate that the governmental regulation succeeded to minimize new hydrocarbons inputs specially in the touristic studied sites. The presence of high concentrations of n-alkane (n-C_{25}) causes this confusion is an indication of biogenic origin [2].

(4) *Un-resolved complex mixture /Resolved (U/R ratio)*, UCM or hump of un-resolved hydrocarbons is one of the more convincing indication of the petrogenic origin and the extent of weathering and biodegradation [20]. The ratio of un-resolved to resolved components U/R has been calculated for most samples and was found to be >4. This value is a criterion for the presence of important petroleum residue [2]. Winter water samples show values between 0.438 to 1.642 (Table 8) which means that the presence of dispersed oil from recent oil inputs. On the contrary, summer samples display values ranged between 0.975 to 19.91 due to high concentration of aromatic and naphthenic compounds.

3.3. FT-IR Technique

The IR spectra for the oils extracted from seasonal water samples are presented in Figure. 5. The characteristic bands for aliphatic hydrocarbons appear as a strong band at 2923 and 2853cm^{-1} due to stretching vibration of methylene groups (Vas CH2) and (Vs CH2) stretching vibration, respectively[21]. Strong bands at 1462 cm^{-1} due to (δas CH3) bending vibration of CH3 group and medium band at 1374 cm^{-1} due to (δsCH3) bending of CH3 group [16]. Medium band at 730 cm^{-1} due to out of plane bending of =C-H group in mono and poly-nuclear aromatics. Indeed strong band at 1732 cm^{-1} due to carboxylic esters [3]. Finally, a medium band at 810 cm^{-1} is significant for naphthenic aromatics compounds[8].

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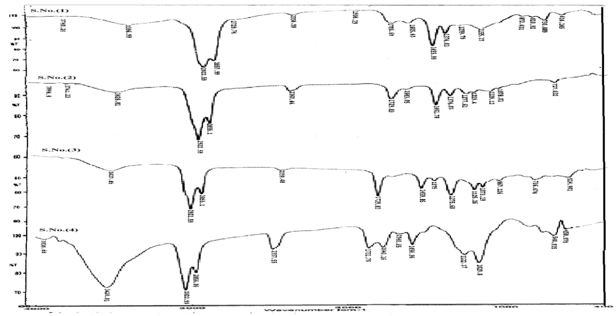

Figure 5. FT-IR absorption spectra for some selected seasonal water samples

4. Conclusions

The present investigation evaluated various ratios and indices to assess the level and sources of petroleum hydrocarbon contamination in Suez Gulf surface water samples. The concentration of Physicochemical parameters were found to be relatively higher than the recommended in the regulations of the *Egyptian low of Environment of No*.4/1994. The extracted oils show that *n*-alkanes are standing out equal distances above a relatively moderate hump of un-resolved complexes mixture (UCM) and display a bimodal *n*-alkanes distribution significant for mixed crude oil or tank washing. CPI values in the more than 1, however suggest a mixed contribution of hydrocarbons from both anthropogenic and natural sources. FT-IR spectroscopic analysis indicates high concentrations of aliphatic hydrocarbons as well as mono and poly –nuclear aromatic hydrocarbons in addition to naphthenic compounds. The data gathered suggest that the level of hydrocarbons recorded in water matrices are more significantly from industrial, domestic wastes discharge, storm waters, urban runoff and other anthropogenic sources other than oil spillage. The pollution level is generally adjudged to be minimum; nevertheless there is need for frequent evaluation and strict enforcement of the environmental laws relating to occasional oil spillage and waste disposal in the study site.

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