

Assessment of Contamination by Petroleum Hydrocarbons in Sediments along Discharge Basin of Suez Oil Refinery Company, Southwest of the Suez Gulf

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THE PRESENT study was performed in discharge basin of Suez Oil Petroleum Company (SOPC), which is located southwest of the Suez Gulf. Sediment samples were collected from this area and investigated in 2012 - 2013 by Gas chromatography, Ultraviolet, and FT-IR spectroscopy. Gas chromatography analysis revealed petrogenic pollution and traces of biogenic hydrocarbons could also be detected. The concentration of total alkanes and unresolved complex mixture (UCM) in sediment samples ranged from 1116.3 up to 2137.4 $\mu\text{g/g}$ with average 1638.683 $\mu\text{g/g}$ dry weights, the discharge of hazardous materials such as petroleum and chemical solvents to the aquatic environment has become the focus of increasing regulatory and public concern because of the adverse impacts of such materials on human health and the environment; Petroleum concentrations as low as 0.1 ppm have been shown to be acutely toxic. As the concentration was greater than the natural background concentration; therefore, the region can be considered (highly) polluted. Despite the high concentration of anthropogenic contaminants including industries, processing activities and other non-point source pollution. The unusual results may be related to wastes of conversion operations of crude oil to refined products. The present work demonstrates the complexity of hydrocarbon forensics when applied to chronically contaminated environments.

Keywords: Hydrocarbons contamination, Bottom sediment, Petrogenic, Biogenic, Weathering ratio (WR) and Terrigenous /aquatic ratio (TAR).

Suez Oil Petroleum Company (SOPC) industries include chemical industrial installations and oil production⁽¹⁾ identified a number of hotspots where the sediments polluted by hazardous organic pollutants such as aliphatic hydrocarbons. The major sources of aliphatic hydrocarbons are oil production and other activities in the region. Chemical pollution is limited to the vicinity of industrial zones and facilities⁽²⁾ which usually discharge their effluents: (aromatics, chemicals, fuel) which assemble 40% from local consuming: as solar, (local, banker, electrical station), benzene (80, 90, 92), botogas, mazote by different types and characterization, sulfur (liquid and solid types), asphalt (60, 70) which discharged directly into the Suez Gulf in addition, free product were discharged into outlet of

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SOPC by investigation of these products, it found (paraffin's, isoparaffins, aromatics, naphthenes and olefins) and give a complete breakdown of the entire chemical component which comprise the hydrocarbons. Chemical analysis of the free product collected from the subsurface sediment reverse that several sources of petroleum hydrocarbon release are responsible for the free product plume. Mazot, Solar (diesel) and gasoline (benzene) range petroleum hydrocarbons. Sediments are deposited materials consisting of organic matter, mineral matter and inorganic material of biogenic origin. They are an efficient tool to identify environmental impacts, due to the exposure time to industrial effluents; they are valid for long term studies⁽³⁾. Sediments are considered being pollutant traps which contain a high level of pollutants ready to pass on the food chain or be mobilized by anthropogenic or natural means, so they act as indicators for the relationship between natural and anthropogenic variables. The capacity of sediment may be related to its physic-chemical properties, such as grain size and organic matter. The accumulation of hydrocarbons is more likely to occur in sediments where the water is shallow and both wave and current action is minimal⁽⁴⁾. Environmental pressures derive from high demographic density in the hydrographic basin of the bay in Gulf, the presence of the second major industrial complex in Gulf and the lack of suitable treatment of domestic sewage and of numerous industrial effluents. The bay provides support for activities related to petroleum exploration, transport and processing. Commercial and leisure navigation and urban runoff play a role as well in raising the levels of contamination. Because of the growing influence of fossil fuel production and uses, hydrocarbon derived contamination in the bay has become of special concern. However, for abating inputs of hydrocarbons which pose risk to animal and human health it is essential to identify the major sources to be controlled. Previous works carried out in certain areas of the bay⁽⁵⁾. Aliphatic and polycyclic aromatic hydrocarbons are associated with particulate and dissolved material and tend to be deposited in the sediments⁽⁶⁾. The composition of hydrocarbon compounds found in sediments reflects the relative contributions from different sources: biogenic, diagenetic, petrogenic and pyrogenic⁽⁷⁾. The study of hydrocarbons in estuarine systems is immensely important as these areas are highly productive and receive large amounts of pollutants from terrestrial drainage.

Estuaries are partially enclosed water bodies with a restricted access to the sea. Due to their hydrological-geomorphologic configuration they retain, transform and accumulate a large fraction of terrestrial borne matter, with one of the material export terms being the ultimate burial in the sediments. The hydrocarbons in sediment are used for source identification and the reconstruction of the historical records of these hydrocarbon inputs for environmental impact studies. Oil pollution in sediments and natural petrogenic inputs either from oil seeps or from the erosion of ancient rocks is indicated by several features in hydrocarbon fractions. These features include the presence of the unresolved complex mixture (UCM) and a lack of predominance of an even- or odd-carbon number for *n*-alkanes⁽⁸⁾. Immediately, after the release of crude oil into marine waters, due to the lipophilic characteristics and bio- resistant properties of the petroleum compound, it adsorbs to the suspended particulate matter and accumulates in

bottom sediments, and it can remain unchanged and toxic for long term; thereupon, they can have a long-term effect on the structure of the benthic community⁽⁹⁾. The present study investigates petroleum hydrocarbon pollution, to determine the current level of oil pollution in the sediments of SOPC discharge basin along the Suez Gulf, and also aimed to provide useful data for the environmental assessment initiatives for maritime sector for such future studies.

Materials and Methods

The reagents were all analytical reagent grade or chemically pure. All solvents were redistilled and dried before use by standard procedures^(10,11). All the oils-extracted from sediment samples were analyzed according to the standard test method IP318/75⁽¹⁰⁾.

Area of study on the Suez Gulf

Suez Gulf to be wholly affected by the discharged pollutants (Fig. 1 and 2), outlet of Suez Oil Company is located in area about 2-3 km south west of Suez city and closed to the most important and famous international way⁽¹²⁾. The minimum areas and dimensions for discharge basin as a final design: Number of channel (n) is 2, the maximum Width, (B) = 55m. Depth, (d) = 3.5 m. Length, (L) = 148m. Sampling station have selected to appreciate the direct influence of associated oil activities Suez Gulf relative to a reference background level represented by the discharge basin of (SOPC).



Fig. 1. Map of the discharge basin of SOPC and sampling stations along the Suez Gulf.

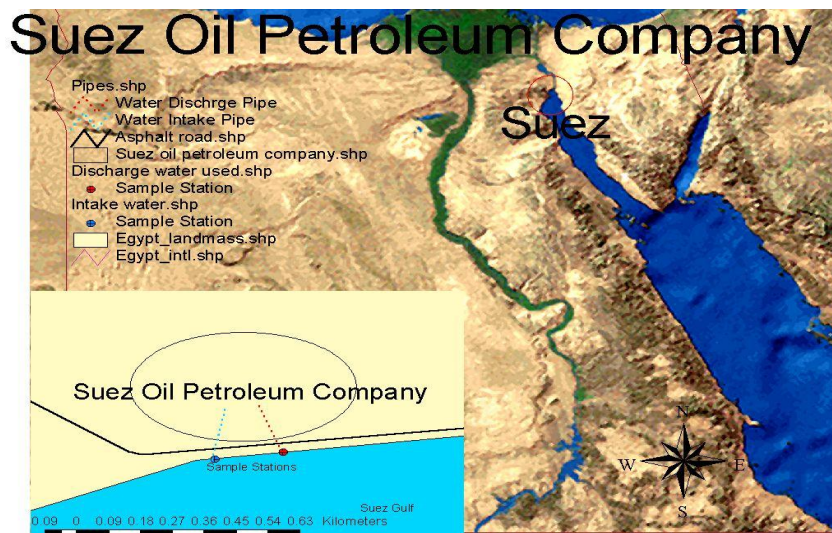


Fig. 2. Position of the Suez Oil Petroleum Company (SOPC).

Samples collection and storage

Surface sediment (0-2cm) samples were collected using a stainless steel grab from different stations along the discharged Basin of (SOPC), according to activities for each site and distance (Table 1), then mixed and stored in refrigerator in pre-cleaned jars until analysis⁽¹³⁾.

Oil extracted from sediment samples

Sediment samples were collected from five stations at different distances along discharge basin of (SOPC). Put 500 g. of dried, sediment in round bottomed flask 300 ml, methanol and 15 g. potassium hydroxide were added. The mixture were refluxed for 1 hr and 30 min then cooled to room temperature. The methanol extracted twice with 25 ml n. hexane, then, the extract was filtered through anhydrous sodium sulphate. The volume was reduced to 0.5 ml. The reduced volume was transferred quantitatively to glass vial. The extracted oil was concentrated to approximately 0.2 ml using dry nitrogen. The oil content in sediment was then calculated after removing the solvent till constant wt.⁽¹⁴⁾.

$$\text{The oil content was calculated as: } \mu\text{g/g} = \frac{(\text{A}-\text{B}) \times 10^6}{\text{Weight of gram of sample}}$$

where: A & B are the weight of bottle after and before action.

TABLE 1. Studied sites, their locations, activities and distance along the drainage Basin of (SOPC).

S. No.	Locations	Activities for each site	Distance along drainage basin (m.)
7	Outlet of Suez Oil Petroleum Company at 100m. /west.	Wastes of conversion operations of crude oil to refined products along the west side of the outlet of petroleum drainage of Suez Company with 100 m. / west.	100m. / west.
9	Outlet of Suez Oil Petroleum Company at 50m. /west.	Wastes of conversion operations of crude oil to refined products along the west side of the outlet of petroleum drainage of Suez Company with 50 m. / west.	50m. / west.
8	Outlet of Suez Oil Petroleum Company at <50m. /west.	Wastes of conversion operations of crude oil to refined products along the west side of the outlet of petroleum drainage of Suez Company with 50 m. /east.	<50m./west.
10	Outlet of Suez Oil Petroleum Company at <50m. / east.	Wastes of conversion operations of crude oil to refined products along the east side of the outlet of petroleum drainage of Suez Company with 50 m. /east.	<50m. /east.
10*	Outlet of Suez Oil Petroleum Company at 100m. / east.	Wastes of conversion operations of crude oil to refined products along the east side of the outlet of petroleum drainage of Suez Company with 100 m. /east.	100m. /east.

M: Meter's

Gas chromatography analysis

All the oils-extracted from the studied sediment samples were analyzed using capillary column according to the standard test method IP318/75^(10, 11) for analysis and testing of petroleum and related products. Agilent 6890 plus, Gas Chromatograph with HP-5,30m0.25mm id, 0.25 μ m film thickness capillary column. The Carrier gas was helium at flow rate of 2ml/min. The injection volume was 0.1 μ l. Oven temperature increased from 80°C with a rate of 3°C/min up to 300 °C. The injector temperature and detector temperature were 320 °C.

Fourier transforms infrared spectral analysis (FT-IR)

This technique was used for the characterization of petroleum and its degradation compounds dispersed in samples. Infrared allows us to give a picture of an oil's health and also whether any contaminants are present such as fuel or coolant. The sample as dissolved in carbon tetrachloride (A.R.) and introduced into quartz cell for analysis. Nicolet IC-10 FT-IR, Thermo Fisher Scientific model Nicolet IC-10, CS-Q 01, AKX0901119012A0607 was used in the range 4000-500 cm^{-1} ^(15, 16).

Ultraviolet analysis

Ultraviolet analysis was carried by UV/VIS/NIR Spectrophotometer (USA) V-570 JASCO. The oil samples extract was dissolved in small amounts of n-hexane, Scanning range 200 – 600 nm, the absorbance (A) was measured and their ratios were calculated as A205/ A215, A228/A256, A248/A267, A248/A278^(17,18).

Results and Discussion

Oil contamination of surface sediment and comparable with some studied reported

Nowadays, petroleum industries are considered as one of the most important basic industries all over the world. Products derived from refining of crude oil are among the most abundant consumer products in the world. Although petroleum industries have too many benefits for our life, the pollution caused by these industries has been a cause for concern and major challenges to save the environment against their adverse impacts all over the world⁽⁹⁾. Immediately, after the release of crude oil into the Suez Gulf, due to the lipophilic characteristics and bio-resistant properties of the petroleum compound, it adsorbs to the suspended particulate matter and accumulates in bottom sediments, and it can remain unchanged and toxic for long term; thereupon, they can have a long-term effect on the structure of the benthic community. Due to the sensitivity of Gulf area, the studies have been performed on various pollutants and primary sources. Five samples have chosen for this study according to their locations, activities and distance taking place in each site along the drainage basin, the main activities which may cause sediment pollution as given in Table 1 and Fig. 1. Variable concentrations for oils extracted from sediment samples ranging between 1116.3 and 2137.4 µg/g.dry weights with average 1638.683 µg/g.dry weights, this indicates that different hydrocarbon levels are contaminating different sites along the discharge basin according to distances. Table 2 displays the lowest values at sites (7) 1116.3 & (10*) 1221.515 µg/g dry weights which extend (100 m.) at west and east sides, respectively along the drainage basin of (SOPC), sites (8) 2137.4 & (10) 2108.666 µg/g.dry weights display nearly values and higher than other due to these sites are located at (<50 m.) along the drainage basin from the west and east sites, respectively, beside site (9) reverse value 1609.536 µg/g.dry weights, which located at (50 m.) from the west side of drainage basin. This is consistent with the direction of the water currents and winds from the west to the east sides at the basin, the high concentration for S.NO. (10*) 1221.515 µg/g dry weights at the east side this attributed to the presence of this site from nearby Petroleum Nasr Company. Generally, the levels of hydrocarbon in the sediment at all study areas depending on distances and sites with the west higher value than the east ones along the discharge basin therefore, the concentrations of oil content decrease with increasing the distance along drainage basin and the stations can be arranged as follows 7<10*<9<10<8 (Fig. 3). At all the petroleum concentrations as low as 0.1 ppm have been shown to be acutely toxic⁽¹⁹⁾. So, the stations, reverse concentration of oil were greatly polluted area, this due continental fraction comes mainly from some oily smuggling occurs for water and discharged via drains along the basin which is caused by refinery production units (Coking - distillation - oils), liquidation warehouses crude and petroleum products, water waste companies neighboring filter

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wards pumps, Trnchat grids crude and petroleum product are assembled this oily water and pushed through a network of lines to basins separated oil during the Suez Oil Processing Company. So, the discharge basin was classified as highly polluted and aliphatic hydrocarbons concentration in sediments was categorized into four levels (guideline $\mu\text{g/g}$): Unpolluted area /natural background level (10-15), slightly polluted area / upper permissible limits (15-50), moderately polluted area (50-200), heavily polluted area^(20,9). By comparing the concentration to other regions of the world (Table 3), levels are shown to be substantially higher than those from selected pristine environments. These high values may point out that high residual petroleum fractions are precipitated on sediments. These residual petroleum fractions of oil cannot be completely treated or degraded easily through weathering processing, consequently, this leads to accumulation of oil residues in sediments. The drainage basin was under stress from intensive wastes of conversion operations of crude oil to refined products along the east and west sides from it. The deliberate drainage of oil related activities and oily smuggling from the industrial processing cause continuous inputs and large cumulative loading on the discharge basin water and bottom sediments.

TABLE 2. Oil content ($\mu\text{g/g}$ dry weight) extracted from drainage Basin sediment of SOPC.

S.NO	Location	Oil content ($\mu\text{g/g}$)
7	Outlet of Suez Oil Petroleum Company (SOPC) at 100m. /West.	11116.3
9	Outlet of Suez Oil Petroleum Company (SOPC) at 50m. /West.	1609.536
8	Outlet of Suez Oil Petroleum Company (SOPC) at <50m. /west.	2137.4
10	Outlet of Suez Oil Petroleum Company (SOPC) at <50m. /east.	2108.666
10*	Outlet of Suez Oil Petroleum Company (SOPC) at 100m. /east.	1221.515

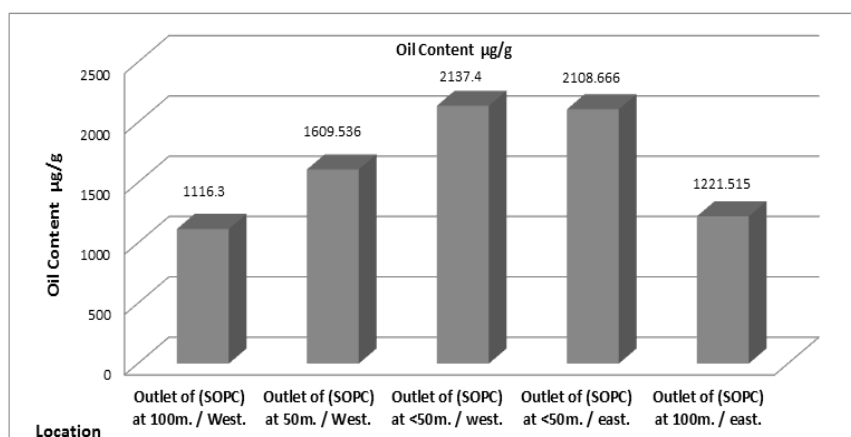


Fig. 3. Histogram representing oil content concentration ($\mu\text{g/g}$ dry weight) extracted from drainage Basin of SOPC.

TABLE 3. Comparison between levels of petroleum hydrocarbons in sediments ($\mu\text{g/g}$) from different regions of the marine environments.

Area	Site	Range ($\mu\text{g/g}$)	Mean	Guideline ⁽⁹⁾	References
Suez Canal	Suez Canal	2.91-127.7	32.37	10-15	(21)
Suez Canal	Suez Canal	0.04-2.45	32.37	10-15	(22)
Red Sea	Saudi Arabia Coast	10.3-803	326.9	10-15	(23)
Mediterranean Sea	Damietta Harbor	0.16-4.16	1.44	10-15	(24)
Black Sea	Monaco	2.1-310	59.656	10-15	(13)
Mediterranean Sea	Damietta – Port Said	15.50-100.2	48.8	10-15	(11)
Mediterranean Sea	Damietta – Man zalah lake	121.5-579.9	260.632	10-15	(15).
Mediterranean Sea	Alexandria, Egypt	14.3-170.4 summer) 12.1-107.9 (winter)	55.342 27.145	10-15	(25).
North Africa, Spain	Ceuta harbor:	496- 6972	3331 \pm 2317	10-15	(26).
Candarli Gulf	Turkey	3.88 - 24.7	8.695	10-15	(27).
Musa Bay,	Northwest of the Persian Gulf- Iran	17.51-88.81	45.94	10-15	(9).
Mediterranean Sea	EL- Man zalah lake	5.0-132.5	-----	10-15	(28)
Suez Gulf	Discharge Basin of (SOPC)	1116.3- 2137.4	1638.683	10-15	This work

Gas chromatographic analysis (GC)

Gas Chromatographic Analysis (GC) for oil extracted from sediments is achieved for severely weathered oils and refined products not only *n*-alkanes but also branched and cyclo-alkanes are heavily or completely lost and the UCM becomes extremely pronounced, resulting in significant increase in relative ratios of UCM/GC- TPH, and in a substantial decrease in relative ratios of resolved peaks to GC- TPH ⁽²⁹⁾. The studied sediment samples gave chromatogram similar to those for petroleum weathered profiles consisting of a number of *n*- alkenes peaks starting from *n* C₁₁ up to *n* C₃₆ for the samples (Fig. 4 and Table 4). Also, the chromatograms profile is characterized by the presence of relatively large UCM hump with small peaks shows the different degrees of weathering effect in all samples, and the absence of low molecular weight hydrocarbons in most samples. It is clear that all samples are contaminated by petrogenic origin hydrocarbons (regularly spaced small peaks over well defined UCM) are shown in Biogenic sources for hydrocarbons indicated by the dominance of *n*-alkanes (*n*C₁₇, *n*C₁₉, *n* C₂₅, and *n*C₂₉)^(28, 30), which are synthesized by marine algae and higher terrestrial plant waxes. The paraffinic hydrocarbons are shown to decrease regularly to different extents indicating various degrees of weathering.

*GC- parameters**Carbon preference index (CPI)*

An unresolved complex mixture (UCM) occurring in the range $nC_{18} - nC_{35}$ is an indicator of petroleum contamination⁽³¹⁾. In order to determine the natural or anthropogenic origin of the *n*-alkanes, the carbon preference index (CPI) was calculated as the sum of the odd carbon numbered alkanes to the sum of the even carbon numbered alkanes, CPI indexes were determined for each sample set (Table 4). CPI indicated the relative contributions from natural sources (biogenic/terrestrial; $CPI > 1$) and anthropogenic sources (petroleum pollution and highly degraded of organic matter, $CPI \approx 1$) at station (8). Each sample has CPI values maximized is as higher plant inputs drastically increased through rain drains⁽³²⁾. CPI data of sediment samples ranged from 0.071 to 0.974, 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 (1.00)^(18, 33), the presence of high concentration of *n*-paraffin (nC_{25} or nC_{23}) causes this confusion gave an indication of the biogenic origin⁽¹⁶⁾. The CPI values were calculated again without taking in consideration the value of nC_{25} or nC_{23} peak areas. Table 4, shows the results for the CPI correct values ranged from 0.046 to 0.872. These indicate that the petrogenic origin is mainly predominating, while little biogenic contaminations can be detected especially that of nC_{25} .

Unresolved / resolved complex mixture 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^(30, 34). The ratio of un-resolved to resolved components U/R has been calculated for most samples usually $U/R > 4$ is used as a criterion for the presence of important petroleum residue^(35, 36). Table 4 for sediment samples show values between 2.757 to 16.765 due to high concentrations of aromatic and naphthenic compounds. The high values of the UCM in sediment samples, as with those obtained in the present study, have been reported as evidence of chronic oil-pollution.

n- Alkanes quantization results

The aliphatic hydrocarbon distribution consisted of resolved compounds (mostly *n*-alkanes) and an unresolved complex mixture (UCM)⁽¹⁶⁾. The distributions of *n*-alkanes are shown in Fig. 4. An UCM, consisting of branched and cyclic hydrocarbons, was present in all samples. The UCM indicated that more pronounced petroleum-related inputs occurred at the distances of sampling sites along discharge basin; industrial complex of the petroleum Suez Company and different activities' processing appeared then to be the major sources of such inputs in the study area. Careful examination of Table 4 and Fig. 4 illustrates that total alkanes percentage concentration of pollutants from samples sites 8, 10, 10* & 9 ranges from 5.629 to 9.087% whereas, aromatic and cyclic compounds percentages ranges from 90.913 to 94.371% including a significant hump representing large amounts of UCM from naphthenic and aromatic compound. 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⁽³⁷⁾.

Weathering ratio (WR)

Evaporations and dissolution effects are detected by calculating both (WR) $\Sigma nC_{23}-C_{34} / \Sigma nC_{11}-nC_{22}$ and $<nC_{17}/\text{total alkanes}$ ⁽¹⁶⁾. From Table 4, $<nC_{17}/\text{total alkanes}$ range between 0.041 to 0.562, also (WR) have variable values showing different degrees of weathering ranged from 0.098 up to 0.468. These variations indicate various industrial complex of the Petroleum Suez Company as a result of activities processing and discharged of the different pollutants to the Company discharge basin.

$nC_{14}-nC_{18}/\text{five isoprenoid}$

This ratio of *n*-alkanes / iso-alkanes 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⁽³⁵⁾. Data obtained in Table 4, show that this ratio varies from 0.330 up to 91.742 for surface sediment samples. Low value observed for S.NO.10 (0.330) while, S.NO.7 & 10* display relatively high values 9.174 & 2.733, respectively due to being less weathered compared with other samples. Also, sample 8 (0.641) exhibits low value due to extensive weathering, indicating the same degree of weathering due to photo-oxidation, vaporization and biodegradation processes along the discharge basin.

Tn. alkanes/ Tiso –alkanes

Normal alkanes are usually degraded more rapidly than the isoprenoid alkanes⁽³⁸⁾. So this ratio is used as an index for the degree of weathering (mainly biodegradation). This ratio decreases with increasing weathering. Table 4 shows the following sequence: $7 < 10^* < 8 < 10 < 9$, for weathering effects. The relatively higher differences between sequences are due to the differences in the added biogenic hydrocarbons specially that of nC_{25} .

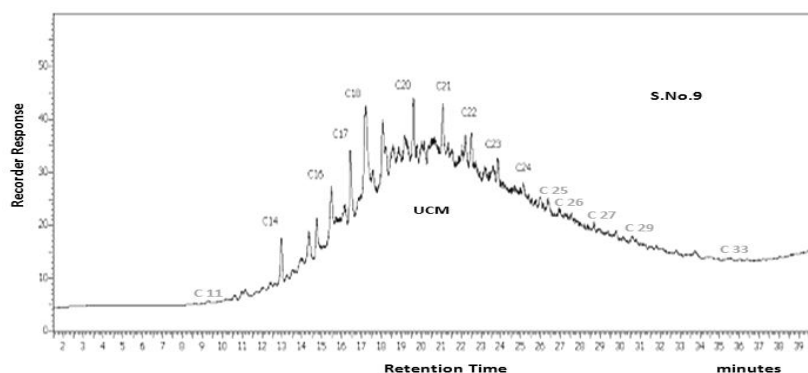


Fig. 4. GC chromatogram of extracted oil of sample no. 9 as an example of GC analysis.

The ratios of (LMW) low molecular weight to (HMW) high molecular weight

A total of 26 aliphatic hydrocarbons (nC_{11} – nC_{36}) were measured for all sediment samples. The concentrations of total aliphatic hydrocarbons ranged from 11.930 to 78.510 ng/g (dry weight) Table 5 and exhibited large variation among stations. Highest concentrations occurred at the station 7 and lowest one was found in S.NO.10. It appears that for all stations except stations 10*, the concentrations of nC_{10} to nC_{20} hydrocarbons were more concentrated than the longer chain (>20) *n*-alkanes. The ratios of low molecular weight (LMW, sum of nC_{10} to nC_{20}) to high molecular weight (HMW, sum of nC_{21} to nC_{34}) LMW/HMW *n*-alkanes are indicated in Table 5. It has been reported that LMW/HMW ratios that are less than unity (1) usually represent *n*-alkanes produced by higher plants, marine animals and sedimentary bacteria, while LMW/HMW ratios close or greater than unity suggest *n*-alkanes that are mainly from petroleum and plankton sources^(40,41). As summarized in Table 5, the LMW/HMW ratios are all greater than unity for most samples, except station 10*, indicating the presence of *n*-alkanes in the sediments is mainly from petroleum-originated contaminations. Aliphatic hydrocarbons diagnostic ratios were studied in order to identify contamination sources. According to the scientific literature many ratios of selected molecular species can be used.

The Pr/Ph, nC_{17}/Pr and nC_{18}/Ph ratios

In this study the Pr/Ph, nC_{17}/Pr and nC_{18}/Ph ratios were adopted and calculated (Table 5), the nC_{17}/Pr ratios, in the range of 0.136–2.295, nC_{18}/Ph 0.050–2.630 and Pr/Ph 0.207–2.025. Overall, the nC_{17}/Pr , nC_{18}/Ph and Pr/Ph values are higher than 1 for all sediment samples. These results show a possible petrogenic origin for hydrocarbons in effluents^(42,43).

Terrestrial hydrocarbons

The study of hydrocarbons based on the analysis of biogeochemical markers as well as the different tracers of origin permits to distinguish two main origins: biogenic and anthropogenic. The important presence of the nC_{15} , nC_{17} , and nC_{19} is strongly assigned to a marine biogenic origin relative to the phytoplankton⁽¹⁸⁾. Terrestrial hydrocarbons are characterized by elevated concentrations in compounds that have high molecular weights and odd carbon numbers, such as nC_{31} , nC_{33} , and nC_{35} . The distribution of odd/even carbon numbers for petroleum-related pollution, however, is relatively even (Table 5). The ratio of terrigenous-to-aquatic *n*-alkanes were estimated as terrigenous/aquatic ratio (TAR) = $(nC_{27} + nC_{29} + nC_{31}) / (nC_{15} + nC_{17} + nC_{19})$ ^(44,45, 27). This ratio is valuable for determining changes in relative contributions of organic matter from land and aquatic flora although it may over-represent the absolute amounts from terrigenous sources. This ratio was adopted in the present study to estimate the relative contribution of terrigenous and processing refiner's sources to the sediments. Station 7 showed comparatively high TAR value 1.595 among the five sediment samples along the drainage Basin of SOPC, which could be caused by input of sediment with high TAR values from the high proportions of relict sediments. The relict sediments presumably have high TAR ratios based on the fact that aquatic *n*-alkanes degrade faster than terrigenous *n*-alkanes.

TABLE 5. Aliphatic hydrocarbon concentrations (ug/g, dry weight) in sediment of the discharge basin of SOPC.

Station Aliphatic hydrocarbons	7	9	8	10	10*
nC ₁₁	N.D.	0.090	N.D.	0.060	0.230
nC ₁₂	N.D.	0.080	0.050	0.140	0.020
nC ₁₃	N.D.	0.080	0.030	0.290	0.050
nC ₁₄	55.94	4.350	2.240	3.150	19.830
nC ₁₅	0.050	0.470	0.460	0.170	1.350
nC ₁₆	0.160	2.530	1.840	0.270	0.810
nC ₁₇	0.080	1.070	0.110	0.210	1.400
<i>Pristane</i>	0.070	0.550	0.810	0.100	0.610
nC ₁₈	4.320	3.060	0.020	0.710	1.080
<i>Phytane</i>	N.D.	2.660	0.400	0.270	1.010
nC ₁₉	0.980	3.790	3.520	0.970	2.300
nC ₂₀	4.720	1.300	0.490	1.150	0.900
nC ₂₁	0.290	1.360	0.080	0.240	0.070
nC ₂₂	2.660	2.080	0.240	1.160	1.280
nC ₂₃	0.340	0.190	0.660	0.750	0.450
nC ₂₄	2.53	1.070	0.920	0.690	0.310
nC ₂₅	1.810	0.960	0.770	0.550	0.470
nC ₂₆	0.520	0.740	0.580	0.400	0.780
nC ₂₇	0.810	0.030	0.310	0.380	0.120
nC ₂₈	0.780	0.480	0.400	0.060	0.620
nC ₂₉	0.600	0.570	0.450	0.130	0.420
nC ₃₀	0.410	0.310	0.230	0.010	0.130
nC ₃₁	0.360	0.160	0.250	0.120	0.280
nC ₃₂	0.390	0.120	0.090	0.130	0.080
nC ₃₃	0.180	0.550	0.03	0.170	0.010
nC ₃₄	0.260	N.D.	0.09	0.010	N.D.
nC ₃₅	0.200	N.D.	N.D.	0.010	N.D.
nC ₃₆	0.120	N.D.	N.D.	N.D.	N.D.
nC ₁₇ /Pr	1.143	1.945	0.136	2.100	2.295
nC ₁₈ /Ph	N.D.	1.150	0.050	2.630	1.069
Pr/Ph	N.D.	0.207	2.025	0.370	0.604
TAR	1.595	0.143	0.211	0.467	0.162
LMW	66.25	13.030	9.84	7.120	27.970
HMW	11.94	12.390	5.100	4.800	32.990
LMW/HMW	5.549	1.052	1.292	1.483	0.848
Total Aliphatic	78.510	25.420	14.940	11.930	32.99

T.*n*-ALK: total resolved *n*-alkanes from nC₁₁ to nC₃₆ with two isoprenoids, pristane and phytane. (pr): Isoprenoids (pr): pristane and (ph); phytane, nC₁₇/Pr.: normal alkanes of nC₁₇ over pristane, nC₁₈/Ph.: normal alkanes of nC₁₈ over phytane, Pr/Ph: pristane (Pr) over phytane (Ph) ratio; TAR: terrigenous/aquatic ratio = (nC₂₇ + nC₂₉ + nC₃₁) / (nC₁₅ + nC₁₇ + nC₁₉); LMW/HMW: the ratios of low molecular weight (LMW, sum of n-C₁₀ to n-C₂₀) to high molecular weight (HMW, sum of n-C₂₁ to n-C₃₄)⁽³⁹⁾, N.D.: Under the limit of detection.

UV spectral analysis

The UV Spectrophotometer (USA) technique, V-570 JASCO modeling, and hydrocarbon composition were used to characterize oil components and to examine the oil extracted from sediment under controlled laboratory conditions (Fig. 5). The spectra for the studied samples show significant bands at 205, 215, 248, 256, 267 and 268 nm. This denotes that different aromatic classes are present in the extracted oils⁽⁴⁶⁾. The recommended four major absorption ratios were identified, at 205/215, 228/256, 248/267, and 248/278 nm, respectively (Table 6). An average was determined for the oil components based on UV Spectrophotometer and hydrocarbon composition measurements, the first ratio 205/215⁽¹¹⁾ pointed generally higher values relative to the other three ratios 228/256, 248/267, and 248/278 nm, ranging between 0.8986 up to 1.0299 ug/g. This indicates high concentrations of mono-aromatic hydrocarbons, compounds such as benzene, toluene and xylene that may be not lost during weathering process, due to continuous inputs of freshly particular oil. Good matching between the studied samples in this range, indicating that low molecular weight aromatics have nearly identical values. The second ratio 228/256⁽⁴⁷⁾, is constant for oil and independent on oil concentration, displayed values between 0.8440 and 0.9228ug/g which reveal different sources of oils polluted these areas. The third ratio 248/267 has values varying between 0.8187 up to 0.8892 with averaging 0.8659 ug/g. This ratio is significant for di-aromatic hydrocarbons. The last ratio 248/278 ranging from 0.6350 to 0.7240ug/g averaging 0.6879 ug/g indicating the presence of different types of poly-aromatics, these compounds are described as the most carcinogenic components, which have great toxic and harmful effects.

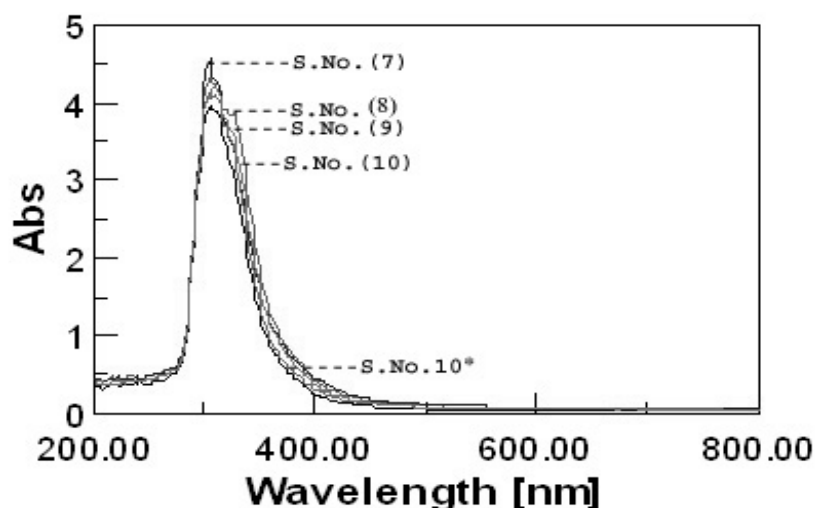


Fig. 5. UV absorption spectra for oils extracted from sediment of drainage Suez Company.

TABLE 6. Calculated UV absorption ratios for oils extracted from sediment of drainage Basin of SOPC.

S.NO.	Location	A205/ A215	A228/ A265	A248/ A267	A248/ A278
7	Outlet of Suez Oil Petroleum Company at 100m. /West.	1.0299	0.8440	0.8718	0.6879
8	Outlet of Suez Oil Petroleum Company at 50m. /West.	0.8986	0.8893	0.8892	0.7240
9	Outlet of Suez Oil Petroleum Company at <50m. /west.	1.0137	0.8902	0.8676	0.6955
10	Outlet of Suez Oil Petroleum Company at <50m. /east.	1.0578	0.9118	0.8821	0.6972
10*	Outlet of Suez Oil Petroleum Company at 100m. /east.	0.9614	0.9228	0.8187	0.6350

A: Absorbance.

FT- IR spectral analysis

- The IR spectra for the oils extracted from sediment samples are presented in Table 7 and Fig. 6. The characteristic bands for aliphatic hydrocarbons appear as a strong bands at 2923 and 2859 cm^{-1} due to stretching vibration of methylene groups (Vas CH_2) and (Vs CH_2) stretching vibration, respectively⁽⁴⁸⁾.
- Strong bands at 1456 cm^{-1} due to (δ as CH_3) bending vibration of CH_3 group from aliphatic hydrocarbons, and medium band at 1375 cm^{-1} due to (δ s CH_3) bending of CH_3 group⁽³⁸⁾.
- Medium band appear at 753 cm^{-1} due to out of plane bending of =C-H group in mono and poly-nuclear aromatic^(49, 18). Indeed, an intense band in the region of 1700 cm^{-1} was observed for the naphthenic acidic fractions, indicating that there was an increasing concentration of acid species⁽⁵⁰⁾.
- Finally, a medium band at 813 cm^{-1} was significant for naphthenic aromatic compounds, (CH aromatic out of – plane deformation, 2 or 3 adjacent free hydrogen atoms)⁽⁵¹⁾.

TABLE 7. Infra red signals and assignments of the oil extracted from the surface sediment.

Wave number cm^{-1}	Assignments of chemical groups
2923	A stretching vibration of methylene groups (Vas CH_2)
2859	A stretching vibration of methylene groups (Vs CH_3)
1462	δ as CH_3 bending stretching of vibration of CH_3 group
1375	δ s CH_3 bending stretching of vibration of CH_3 group
735	out of plane bending of =C-H group in mono and poly-nuclear aromatics
810	significant for naphthenic aromatic compounds
1700	C=O stretching in carbonyl group

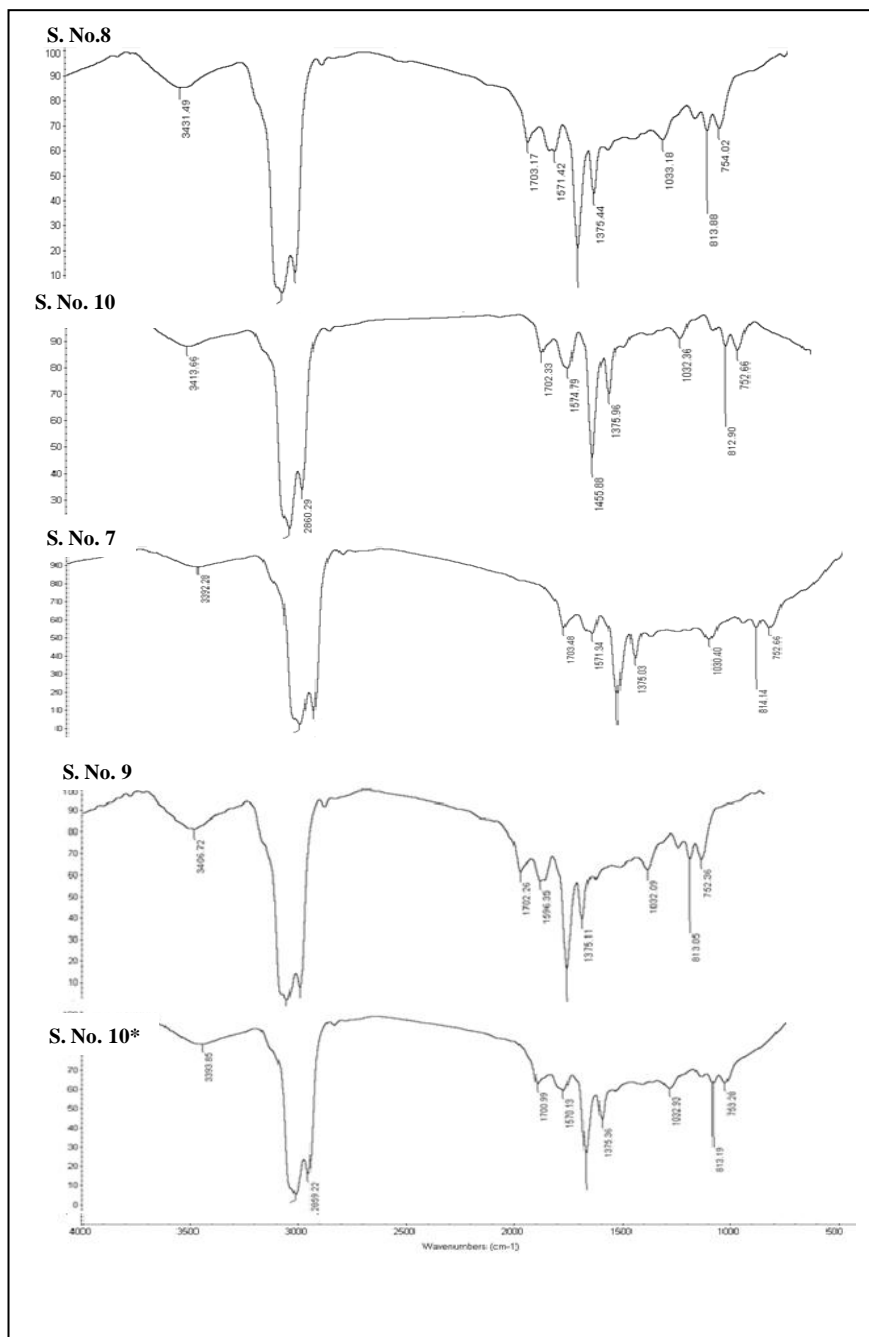


Fig. 6. FT-IR absorption spectra for oils extracted from sediment of drainage Basin of SOPC.

Conclusion and Recommendations

1. In the present work, we attempt to present for the first time the distribution and the origin of hydrocarbons in sediments from discharge basin in the Petroleum Suez Company. The *n*-alkanes in the same location have multiple sources: anthropogenic / petrogenic and traces of biogenic hydrocarbons.
2. Total hydrocarbon concentrations were relatively high compared to other coastal sediments and ranged from 1116.3 up to 2137.4 ug/g.dry weights with average 1638.6834ug/g.dry weights.
3. A complex mixture of aliphatic hydrocarbons evidences that the concentration was greater than the natural background concentration; therefore, the discharge basin can be considered (highly) polluted, this is due to the deliberate drainage of oil related activities and oily smuggling from the industrial processing which cause continuous inputs and large cumulative loading on the discharge basin water and bottom sediments, without completely treated or degraded easily through weathering processing.
4. Despite the high concentration of anthropogenic contaminants including industries, processing activities and other non-point source pollution. The present work demonstrates the complexity of hydrocarbon forensics when applied to chronically contaminated environments.
5. The high values of the UCM due to high concentrations of aromatic and naphthenic compounds have been reported as evidence of chronic oil-pollution.
6. CPI values indicate that the petrogenic origin is mainly predominating, while little biogenic contaminations can be detected especially from *n*C₂₅. This could indicate a potential of biodegradation which is not encountered in the more polluted stations.
7. Hydrocarbons were deposited on surface sediments from a variety of processing sources: an industrial effluent in the discharge basin as a result of oily smuggling occurs with water.
8. Hydrocarbon distribution is an important and useful tool in organic geochemistry studies. UV analysis for oils incorporated in sediments reveals that oil pollutants have considerable amounts of aromatic compounds.
9. FT-IR spectroscopic analysis indicates high concentrations of aliphatic hydrocarbons as well as mono and poly-nuclear aromatic hydrocarbons in addition to naphthenic compounds.
10. The discharge of hazardous materials such as petroleum and chemical solvents to the aquatic environment has become the focus of increasing regulatory and public concern because of the adverse impacts of such materials on human health and the environment; petroleum concentrations as low as 0.1 ppm have been shown to be acutely toxic .
11. Commitment to Environmental Law for the year 1994 on the protection of water and beaches, and which is required to address the wastes within companies before being discharged to the drainage basins, and control in preventing the diversion of oily water by separating oils and which are subject to the standards of permissible concentrations globally.

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تقييم التلوث بواسطة الهيدروكربونات البترولية في الرواسب على طول حوض تصريف شركة السويس لتكرير البترول ، جنوب غرب خليج السويس

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معهد بحوث البترول - مدينة نصر - القاهرة - مصر.

شركة النفط بالسويس هي أول شركة وطنية لتكرير البترول في مصر ، منذ عام 1921، النشاط الرئيسي لشركة السويس للبترول هو تكرير النفط لإنتاج المنتجات النفطية المشتقة مثل النفثالين والكيروسين والبنزين والاسفلت والفحم البترولي والكبريت. وتمتلك الشركة خط إنتاج لإنتاج الفحم البترولي من خلال تزويد أبراج بالفحم فضلا عن الكبريت. وتقوم الشركة بتصريف مياه الصرف الصناعي الزيتي في خليج السويس. وتفيد التقارير أن نوعية المياه من النفايات السائلة غير متفقة مع حدود معايير النفايات السائلة في مصر؛ حيث يحدث بعض التهربات الزيتية للمياه ، يقع مخرج شركة النفط بالسويس في منطقة Zietyia حوالي 2-3 كم جنوب غرب مدينة السويس وتم أخذ العينات من مياه الصرف الصناعي على مسافات على إمتداد حوض الصرف . كانت تركيزات الهيدروكربونات إجمالي مرتفعة نسبيا مقارنة بالرواسب الساحلية الأخرى و تراوحت التركيزات ما بين 1116.3 لتصل إلى 2137.4 ميكروغرام / غرام dry مع متوسط 1638.6834 ميكروغرام / غرام dry . بواسطة مقارنة التركيزات مع مناطق أخرى من العالم أظهرت المستويات تركيزات أعلى بكثير من التي في البيئات البكر المحدد. قد تشير هذه القيم العالية إلى ارتفاع بقايا النفط في الرواسب، هذه البقايا البترولية المتبقية من النفط لا يمكن علاجها تماما ، وبالتالي هذا يؤدي إلى تراكم بقايا النفط في الرواسب. وكان حوض الصرف تحت ضغط من النفايات مكثف من عمليات تحويل النفط الخام إلى منتجات مكررة على طول الجانبين الشرقي والغربي منه. إلى جانب الأنشطة ذات الصلة بتهديب النفط الزيتية من مدخلات مستمرة والتحميل التراكمي كبير على رواسب حوض التصريف؛ مما يؤدي إلى تركيزات أعلى بكثير من المسموح به. تظهر نتائج كروماتوجرافيا الغازان الألكينات في المواقع على إمتداد حوض الصرف لديهم مصادر متعددة من petrogenic والهيدروكربونات الاحيائية Biogenic، وأيضا خليط من Biogenic، petrogenic. يشير التحليل الطيفي لكلا من FT-IR والأشعة فوق البنفسجية UV إلى تركيزات عالية من الهيدروكربونات الأليفاتية وكذلك الأحادية والهيدروكربونات العطرية بولي النووية بالإضافة إلى مركبات النفثالين. لقد أصبح تصريف المواد الخطرة مثل البترول والمذيبات الكيميائية على البيئة المائية محور قلق متزايد من منظمات الصحة العالمية بسبب التأثيرات السلبية لهذه المواد على صحة الإنسان والبيئة ؛ وقد تبين أن تركيزات منخفضة من البترول (0.1 جزء في المليون تكون شديدة السمية. الألتزام بقانون البيئة لسنة 1994 الخاص بحماية المياه والشواطئ ، والذي يلزم بمعالجة النفايات داخل الشركات قبل تصريفها إلى أحواض الصرف ثم بعد ذلك إلى الخلجان والبحار، والتحكم في منع تسريب المياه الزيتية عن طريق فصل الزيوت منها وأن تخضع التركيزات للمعايير المسموح بها عالميا.