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Assessment of the Oil Pollution Extent in the Offshore Sediments, Abu Dhabi, UAE

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Abstract: Among the major threats to the marine environment in UAE is the pollution resulting from the oil and gas exploration, exploitation, transportation via pipelines, loading of oil tanker and downstream conversion in refining and petrochemical operation. The area around Zakum field area has been selected as case study to assess and evaluate the marine oil pollution in the UAE offshore and consequently the Arabian Gulf region. Oil spills cause extensive damage to marine and terrestrial ecosystems, humane health, and natural resources. To effectively determine the fate of spilled oil in the environment and to successfully identify source (s) of such oil and petroleum products, fingerprinting and data interpretation techniques were extensively applied. These include recognition of the distribution patterns of petroleum hydrocarbons, oil type screening and identification, analysis of "source – specific marker" compounds, determination of diagnostic ratios of specific oil constituents, and the application of various statistical and numerical analysis tools.The analytical approaches that have been conducted comprise: grain size analysis of bottom sediments, Total Organic Carbon (TOC), Total Kjeldahl Nitrogen (TKN), Total Petroleum Hydrocarbons (TPH), Polycyclic Aromatic Hydrocarbons (PAHs), the Polychlorinated Biphenyl's (PCBs), total saturates and heavy metals. The issue of how biogenic and pyrogenic hydrocarbons are distinguished from petrogenic hydrocarbons has also been addressed.The study revealed some important results that should be taken into consideration for future monitoring of marine oil pollution. TOC increases from 0.33 wt% to 14.96 wt% towards the northern sector of the field area. TKN ranges from 13.4 mg% to 136 mg% with a marked increase in the central part of the field area. TPH is increasing from 6.14 ppm to 62.7 ppm towards the northern part of the field area which could be classified as slightly polluted area. ∑PAHs is ranging from below detection level to 31.5 ppm with an increasing trend towards the northwestern parts of the field area. Also, it has been recognized in Zakum Field offshore area that hydrocarbons from natural sources including biogenic source are very common in the marine and inland environments. Moreover, there is a wide distribution of the biogenic PAH perylene, as an unsubstituted PAH produced in subtidal sediments by a process known as early diagenesis.

Key words: Pollution, Organic, TOC, PAHs, PCBS; Hydrocarbons, Heavy metals, TKN, Zakum, Abu Dhabi, and UAE.

INTRODUCTION

Marine Pollution can be defined as "the introduction by man, directly or indirectly, of substances or energy into the maritime area which results or is likely to result in hazards to human health, harm to living resources and marine ecosystems, damage to amenities or interference with other legitimate uses of the sea" (Subbarini, 1998). The Arabian Gulf is one of the busiest tanker routes in the world (Al – Lihaibi et al, 1996). Proven recoverable petroleum reserves in these countries are estimated to represent 44 % of the world recoverable reserve (Teresa L. *et al,* 2002). The major sources of pollution in the Gulf countries are related to oil and gas production operations, crude oil spills and leakage, natural gas leakage and flaring, pollutants associated with the refining operation, including refinery wastes and industrial products, by-products and wastes arising mainly from the petrochemical industry (Literathy, 1993). Oil pollution is widespread on the Arabian Gulf region and has seriously endangered the ecosystem (Douabul and Al-Shiwafi, 1998). During the Gulf war in 1991 more than 740 Kuwaiti oil wells were fired, spilled an estimated 10.8 million barrels of crude oil into the Gulf (Tawfiq& Olsen, 1993). It represented the world's largest oil spill (Price, 1998). Proven

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recoverable oil reserves are estimated at about 100 Billion barrels of oil (10 % of the world's total) and 6 Billion cubic meters of natural gas (Teresa L. *et al,* 2002). Zakum field area has been taken as case study to assess and evaluate the marine oil pollution in UAE offshore and consequently the Arabian Gulf. It is located in the central part of the Arabian Gulf about 40 miles northwest of Abu Dhabi town and 62 miles south-east of Das Island. The field was discovered in July 1963 and crude oil production from the Zakum Central Super Complex (ZCSC) commenced in November 1967. The field consists of two zones, the lower zone being operated by Abu Dhabi Marine Operating Company ADMA-OPCO, with Zakum Development Company ZADCO operating the upper zone. The main objectives of this research project are to assess the organic and inorganic pollutants which affect the marine environment, determine the source of petroleum pollution in the marine environment, and to locate the contamination trend and determine its extent.

MATERIAL AND METHODS

Sediment Sampling:

Seabed sediments were collected form 26 stations throughout the Zakum field Area, Abu Dhabi, UAE (figure 1). Bottoms sediments were taken by divers at each sample station and immediately were immediately sealed in plastic bags, refrigerated (> 4 °C) and kept frozen prior to chemical analyses to prevent samples volatile compounds form evaporation and chemical or biological degradation.

Grain Size Distribution Analysis:

The objectives in determining the grain size distribution of sediment is to correlate the level of contaminants special organics to grain size, and determine the percentage of fine particles in the sediment. The grain size analysis was conducted using the standard sieving method as per ROPME (2000) procedure. Statistical parameter of mean size was calculated according to the equation given by Folk (1954).

Determination of Total Organic Carbon (TOC):

Organic matter present in water as individual particulate or as adsorbed matter. Different factors may control the availability of the organic matters and the heavy metal pollutants. These factors include various sediment characteristics, such as grain size distribution, mineral composition and organic content (Al Ghadban *et al,* 1994). The study of the recent sedimentary facies of the Arabian Gulf indicated that the sediments of the northeastern parts contain 0.83-1.51 % organic carbon while the sediments of the northwestern part of the Gulf show lower organic carbon Evans (1966). Organic carbon content was analyzed by treating five grames of selected crushed sediment samples with 10 % HCl to remove carbonates. The washed residue is filtered and about one grame of sample ignited in a Leco Carbon and Sulfur analyzer C – 200.

Total Kjeldahl Nitrogen (TKN):

The nitrogen of amino acids was converted into ammonium sulphate by digested the sample with concentrated sulphuric acid in the presence of a catalyst. Ammonia liberated after neutralizing the acid was steam distilled into boric acid solution and the amount of ammonia was estimated by titration using standard HCL and converted into percent nitrogen. Complete distillation, titration (The distillate is titrating using standard HCL acid with N 0.0241) and calculation is performed automatically using the 2300 KJELTEC Analyzer unit.

Determination of Polychlorinated Biphenyls (PCBs):

Polychlorinated biphenyl's (PCBs) are a class of synthetic chlorinated organic compounds and marketed on the basis of their average level of chlorination under various trade names such as the Aroclor, Askarel and Clophen. The PCBs concentration of the particles ranged from 50 to 350 ng/g^{-1} dry wt, or a mean of approximately 150 ng/g^{-1} these concentrations are higher than have been measured in deep surface sediments and suggest that some decomposition and compound recycling takes place after deposition (Scott W. 1989) invented dates to be include. PCBs were also routinely used in the manufacture of a wide variety of common products such as plastics, paints, pesticides, carbonless copying paper; fluorescent light ballasts. PCBs are the most abundant chlorinated aromatic contaminants in the ecosystem (Borrell, 1993).

Five grams of the solid sediments was mixed with equal quantity of anhydrous sodium sulphate (to absorb the water moisture in the sediments) then was placed in an extraction thimble. Then Approximately 70 ml of the extraction solvent (1:1 Hexane: Acetone) used to extract the sample using automatic soxhlet extraction (2050 SOXTEC, FOSSTECATOR) for two hours (Boiling 1hrs and Rinsing 1 hrs.) then 1 mL was injected to GC/ECD from GC auto sampler 2 mL vial.

Determination of Polyaromatic Hydrocarbons (PAHs):

As a result of the environmental baseline study Phase II on Zakum field indicated that Aceaphthene were the only detected constituents that exceeded a benchmark in the Zakum field area. However the naphthalene detection was isolated to one station, and therefore, it is not widespread throughout the filed (ADMA, 1999). Five grams of the seabed sediment was mixed with equal quantity of anhydrous sodium sulphate (to absorb the water moisture in the sediments), placed in an extraction thimble. The sample was extracted using automatic soxhlet extraction (2050 SOXTEC, FOSSTECATOR) for two hours and fifteen minutes (Boiling 1hrs, Rinsing 1 hrs and evaporation 15 minutes) With approximately 70 ml of the extraction solvent (1:1 Hexane: Acetone). Then the extract was transferred into a concentrator and evaporates under nitrogen to reduce solvent to about 0.5 ml (using TurbonVap Evaporator, Zymark apparatus). Then 5.0 ml of acetonitrile was added and evaporate again till 2 ml was reached. An aliquot of the 20 mL was injected into HPLC, and the PAHs compounds were detected by ultraviolet (UV) and fluorescence detectors simultaneously.

Determination of Total Petroleum Hydrocarbons (TPH):

Total petroleum hydrocarbon inputs to the Gulf are estimated to be 47 times higher on an average basis than the global average (ADMA, 1996). Inputs are mainly attributed to chronic spills from heavy tanker transport activities in the Gulf and from major spills such as those that occurred during the Iran-Iraq war in 1983 and the Gulf war (Al-Ghadban et al., 1994). A 20 g sample of wet sediment was acidified to a low pH i.e. 2 with hydrochloric acid. Mangensum sulfate monohydrate is then added to dry the sample. Then petroleum hydrocarbons were extracted from the sample using Hexane solvent. The residue was weighed then dissolved in fluorocarbon – 113. Infrared analysis of the extract at 2930 cm^{-1} was performed by Nicolet Fourier Transform Infrared (FTR) Magna-IR 560 Spectrometer.

Determination Heavy Metals:

Al Qubaisi (2001) conducted an assessment of meats pollution in sediment of the coastal area in U.A.E. She revealed that the metals concentration on the offshore sediment have a minimum metal pollution accumulation except for those of Ni. A portion of homogeneous sediment sample was accurately weighed (1 g) and digested with acids (30 ml of concentrated HCL and 10 ml of concentrated HNO3) in hot plate up to 120°C to destroy the organic matter and soluble the recoverable elements. After cooling the sample, 100 ml volume with deionized water was made. The solution was placed into Varian Vista MPX-CCD simultaneous ICP-OES with auto fit background correction.

Determination of Mercury:

Five grams of the sediment sample transferred to a closed glass bottle. The sample was digested with nitric acid, sulfuric acid and a dilute potassium permanganate-potassium per sulfate solution for two hours at 95 °C. The digestion oxidizes all forms of mercury to $Hg^{+2.}$ Then Hg^{+2} in the sample is reduced with stannous chloride to elemental mercury which can detected by atomic absorption. The measurement step is performed using Atomic absorption spectrophotometer GBC 906 AA with Hydride generator HG 3000.

RESULTS AND DISCUSSION

Total Organic Carbon (TOC):

The variation and location of TOC % in Zakum filed area at 26 different stations. The organic carbon content ranges between 0.33 % and 14.96 % with average of 4.76 % Fig. 2. The maximum and minimum values were recorded in station no. 7 and 15 respectively. The average TOC % found to be in the range of 4.76 % with higher value than other pervious studies (i.e. 0.46% to 2.8 %) Al Ghadban (1994). From the Fig. 3 it is observed that the north side of the field has higher TOC than other sectors of the field area. It is observed that the north side of the field has the highest TOC content followed by Western east side of the field.

Grain Size Analyses:

Sediment Texture:

The texture of the sediments which taken form the 26 sample station along the Zakum field area is reveled that the most sediments are sandy gravels (Fig. 4).

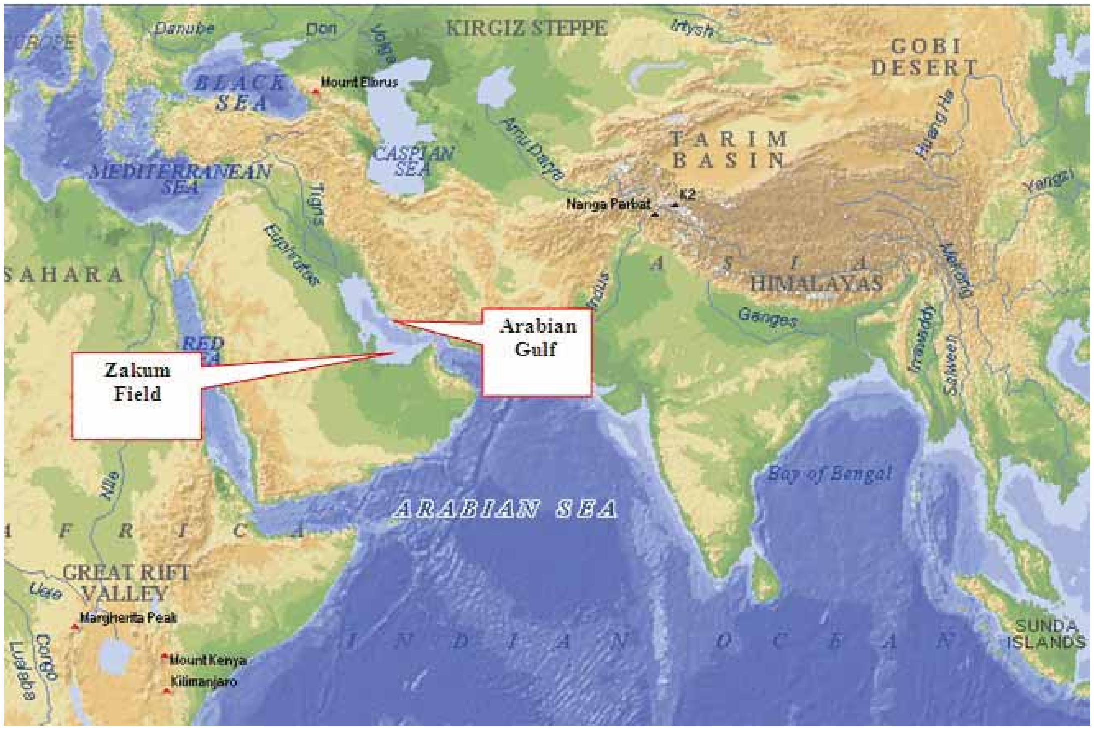


Fig. 1: Arabian Gulf location map.

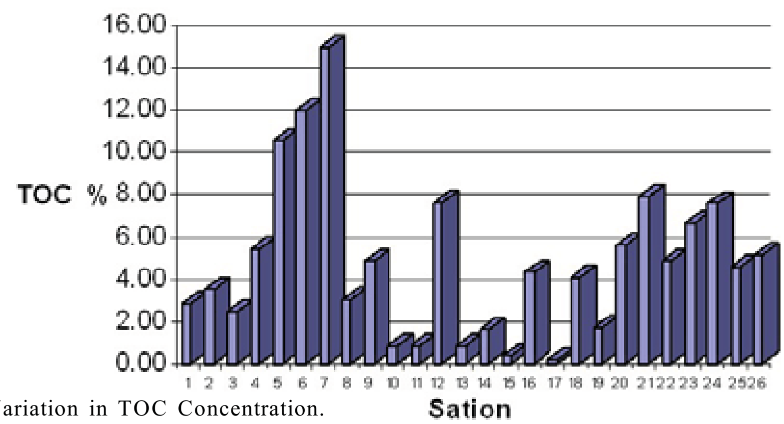


Fig. 2: Variation in TOC Concentration.

Grain Size Distribution:

The mean size of all the 26 samples taken form the Zakum filed area in Phi unit. Most of the samples located in the positive access, which indicated fine to very fine sand, However in four locations there is coarse sand to granule gravel (Fig. 5).

Total Kjeldahl Nitrogen (TKN):

The variation and location of TKN mg % in Zakum filed area at 26 different stations. The Total Kjeldahl Nitrogen ranges between 13.4 mg % and 136 mg% with average of 73.1 mg% (Table I). The maximum and minimum values were recorded in station no. 13 and 25 respectively Figs. (6 and 7).

Total Petroleum Hydrocarbons (TPH):

The variation and location of TPH in Zakum filed area at 26 different stations. The Total Petroleum Hydrocarbons ranges between 6.14 ppm and 62.7 ppm with average of 22.7 ppm (Table I). The back ground

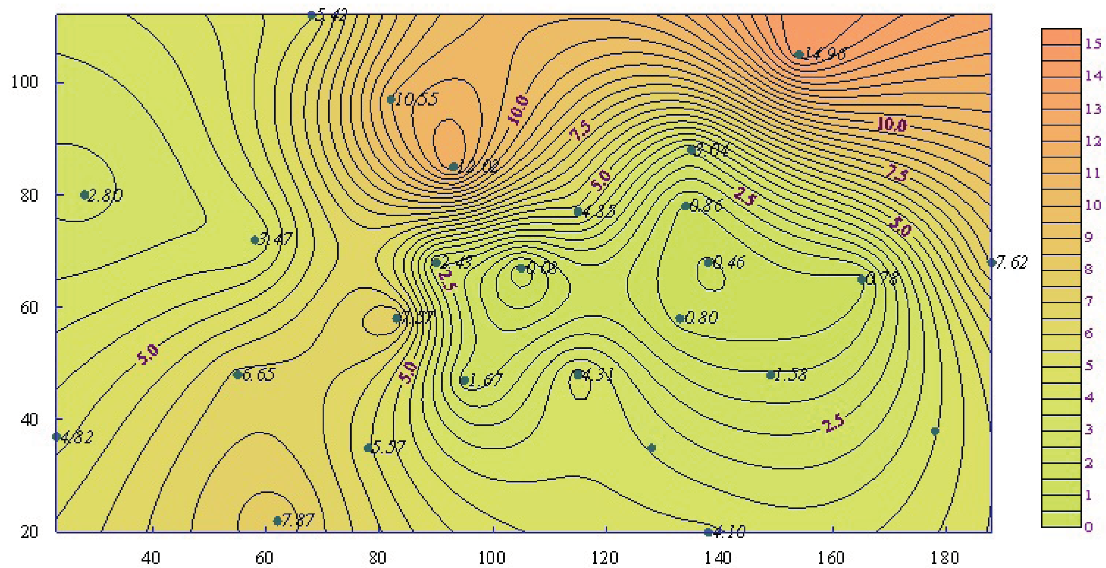


Fig. 3: Contour map of TOC in Zakum Field

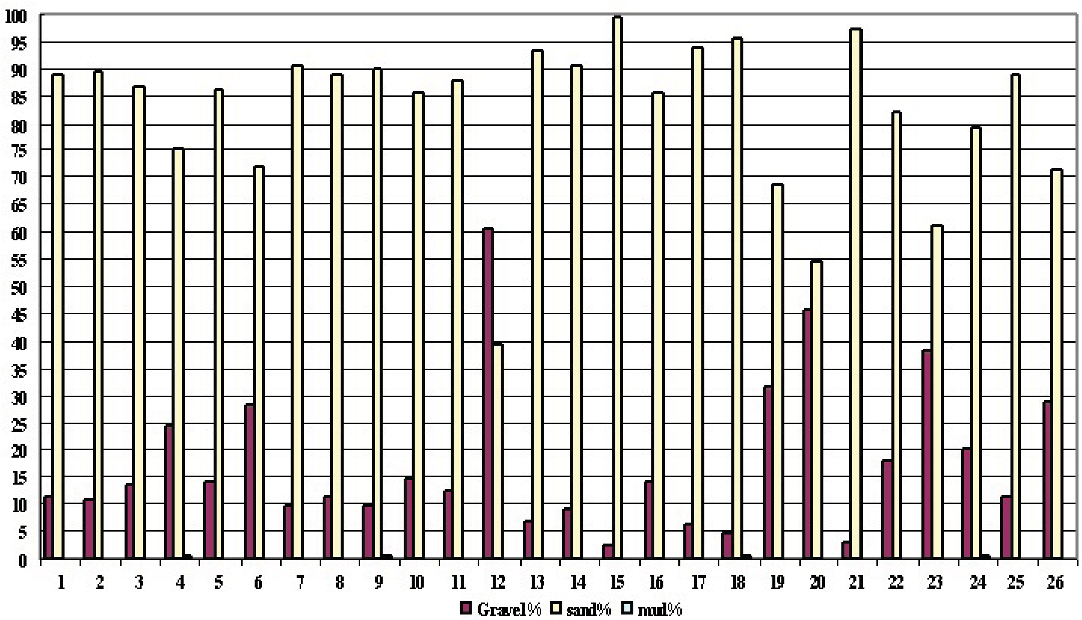


Fig. 4: Sediment Texture of Zakum Field Area

station values show relatively lower TPH concentration with 15.8 ppm and 12.8 ppm. The maximum and minimum values were recorded in station no. 11 and 1 respectively (Fig. 8). From the contour map it is appears that the TPH concatenation increases towards the eastern side (Fig. 9).

Polychlorinated Biphenyl's (PCBs):

The variation and location of PCBs in Zakum filed area at 26 different stations. The Total Polychlorinated Biphenyls ranges between 27.52 ppm and 4.30 ppm with average of 13.5 ppm table (I). The Total PCBs from electrical transformer lube oil in Zakum west super complex found 9.03 ppm. The maximum and minimum values were recorded in station no. 8 and 11 respectively (Figs. 10 and 11).

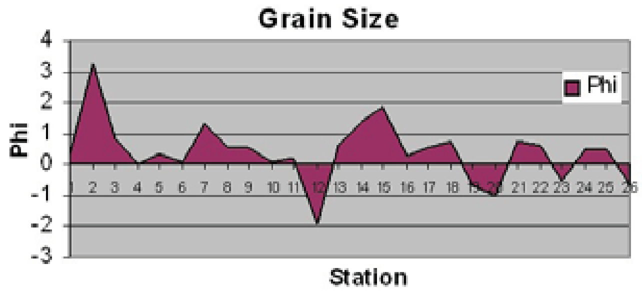


Fig. 5: Sediment Texture of Zakum Field Area.

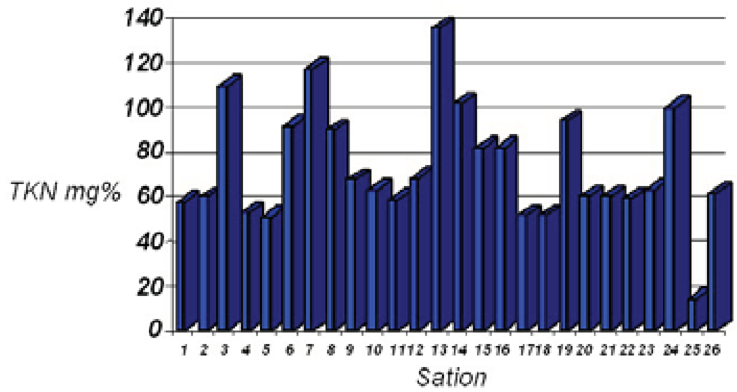


Fig. 6: TKN variation in Zakum field area.

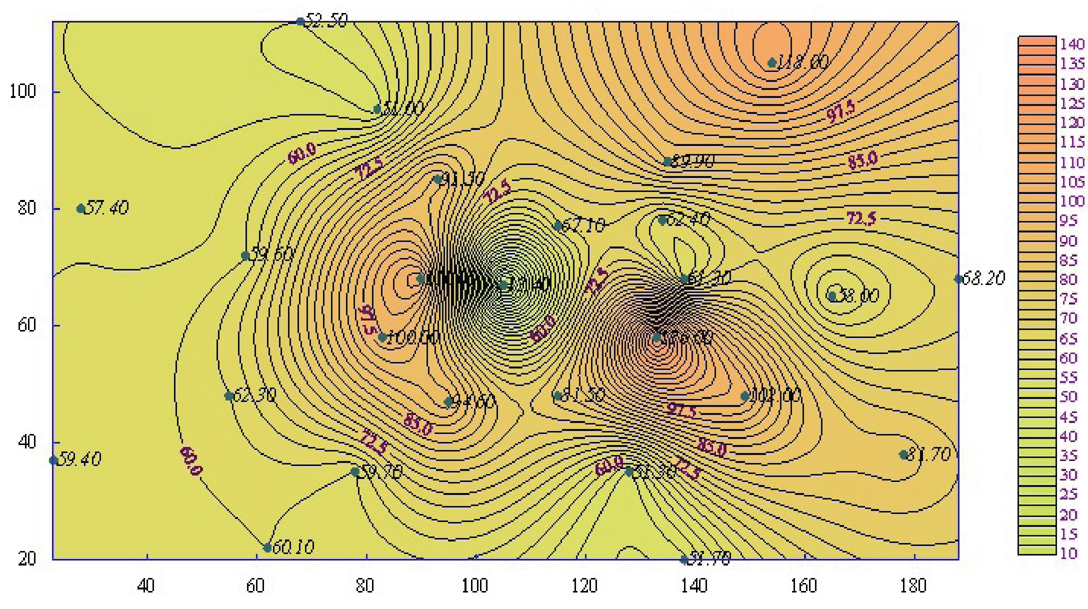


Fig. 7: TKN contour map in Zakum field.

Poly Aromatic Hydrocarbons (PAHs):

The variation and location of total Poly Aromatic Hydrocarbons, PAHs in Zakum filed area at 26 different stations. The Total Petroleum Hydrocarbons ranges between ND ppm and 31.5 ppm (Table I). The maximum value was recorded in station no. 21 (Figs. 12 and 13).

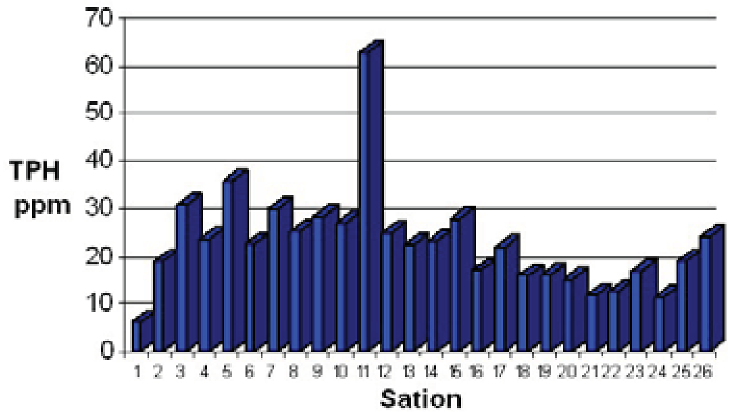


Fig. 8: TPH variation in Zakum field.

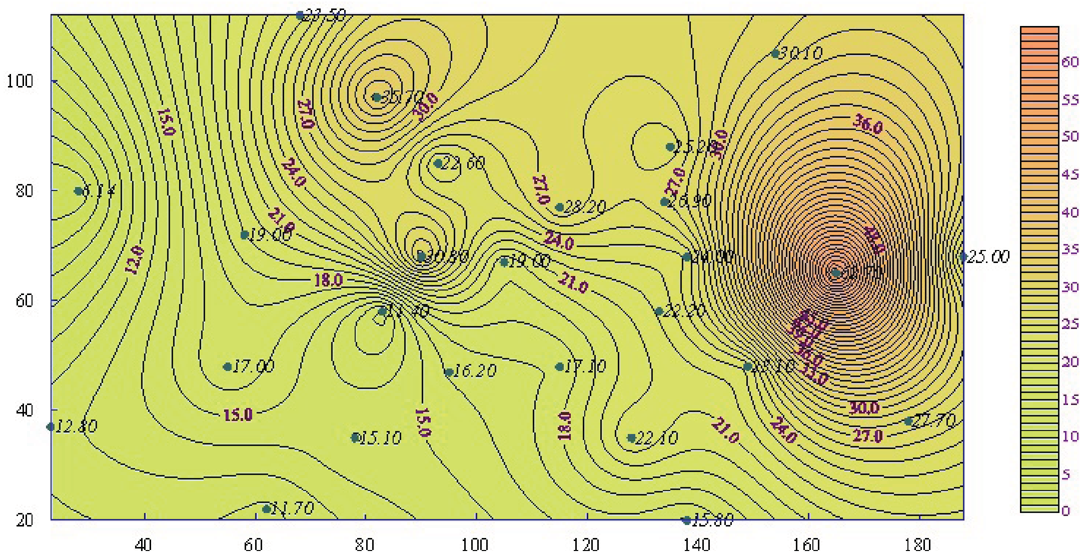


Fig. 9: TPH contour map in Zakum field.

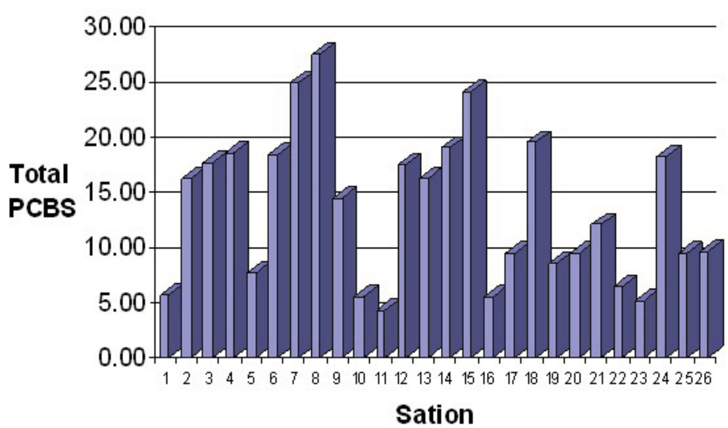


Fig. 10: Total PCBs variation in Zakum field.

Table 1: Concentrations of TOC, TPH, TKN, Total PCBs, and Total PAHs in the studied stations.

Sample ID	TOCwt %	TPH mg/kg	TKN mg/kg	Total PCBs mg/kg	Total PAHs mg/kg
1	2.80	6.14	57.4	5.72	30.7
2	3.47	19	59.6	16.20	21.3
3	2.43	30.8	110	17.63	4
4	5.42	23.5	52.5	18.63	25.6
5	10.55	35.7	51	7.59	0
6	12.02	22.6	91.5	18.36	9.2
7	14.96	30.1	118	24.95	8.8
8	3.04	25.2	89.9	27.52	7.1
9	4.85	28.2	67.1	14.42	11.4
10	0.86	26.9	62.4	5.54	6.1
11	0.78	62.7	58	4.30	0
12	7.62	25	68.2	17.58	0
13	0.80	22.2	136	16.31	7
14	1.58	23.1	102	19.03	15.6
15	0.33	27.7	81.7	24.10	16.3
16	4.31	17.1	81.5	5.52	0
17	0.14	22.1	51.3	9.37	10.9
18	4.10	15.8	51.7	19.59	20.1
19	1.67	16.2	94.6	8.48	15.9
20	5.57	15.1	59.7	9.37	5.8
21	7.87	11.7	60.1	12.05	31.5
22	4.82	12.8	59.4	6.44	12
23	6.65	17	62.3	5.13	8
24	7.57	11.4	100	18.16	0
25	4.57	19	134	9.43	0.08
26	5.15	24	613	9.61	0.59
Average ± S.D	4.77±3.70	22.73±10.65	98.96±107.94	13.5±6.78	10.31±9.49

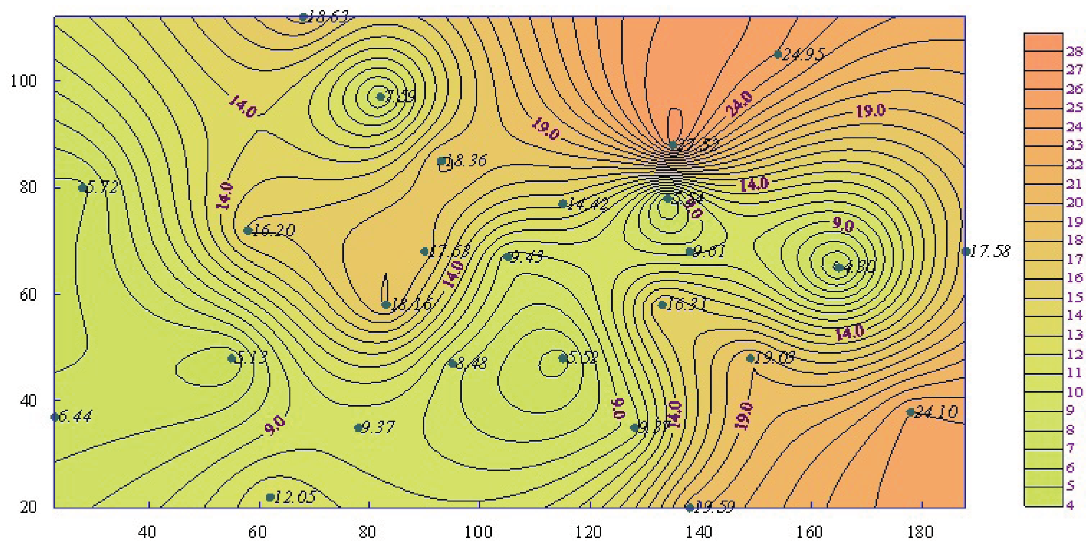


Fig. 11: Total PCBs contour map in Zakum field.

Heavy Metals:

Sediments act as pollutant sinks and provide an integrated picture of the events taking place in the water column. Studies have shown that the hydrocarbons form spilled petroleum persist in the sedimentary environment for a substantial period of times i.e. years. Nine heavy metals elements have been analyses in this study i.e. Ba, Cr, Cu, Fe, Mn, Ni, Pb and Hg. The highest concentration deducted by Fe with total amount of 613.92 ppm (Table II). While the lost concentration deducted by Ni with total amount of 0.91 ppm. Fig. (14) illustrates that the heavy metals could be classified into two main groups: (a) Ca, Sr, Na, Mg which represent lithogenic metals rather than man-made. It attains the high concentrations (b) Cr, Cu, Pb, and Ni which represent the heavy metal associated to the hydrocarbon pollution. It attains the low concentrations. It was found also that association of the high TPH and TOC to the lithogenic metals rather than the man-made (Fig .15).

Table 2: Concentrations of trace elements mg/kg in the studied sediments ND not detected

Sample ID	Al	Ba	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	Sr	V	Si	Hg
1	198.20	6.15	325760	ND	4.12	1.03	416.29	413.81	4690.80	7.82	6465.80	1.46	248.10	0.93	4008.60	3.83	130	ND
2	325.54	13.05	313580	ND	3.92	1.07	501.21	775.94	7461.50	14.02	9077.50	2.28	327.82	0.62	3226.30	2.56	98	ND
3	187.88	24.60	316130	ND	14.20	2.49	317.96	830.37	5838.30	9.41	8627.40	2.18	292.62	1.94	3958.90	2.50	58	ND
4	611.28	31.54	318800	ND	5.82	2.40	880.39	838.97	9542.10	22.36	7917.50	3.84	345.64	1.48	3257.50	4.25	29	15.50
5	344.56	11.40	320730	ND	7.04	0.72	1518.20	473.57	6296.20	13.93	6802.20	1.78	263.08	1.02	3243.60	9.38	77	11.10
6	161.82	17.98	320880	ND	3.79	0.86	342.19	813.09	6731.80	11.59	8236.10	1.39	291.02	0.88	3755.80	3.14	120	ND
7	143.29	22.86	309930	ND	1.78	1.89	281.16	838.17	5094.40	7.84	8615.20	1.26	211.48	0.85	4661.80	2.07	60	ND
8	213.23	17.64	326110	ND	4.93	1.45	589.48	725.43	6107.60	11.48	7744.30	1.39	313.03	1.03	4193.00	4.89	120	ND
9	484.93	21.12	334780	ND	9.33	1.33	1641.50	566.79	8421.10	23.36	6989.10	2.30	318.12	1.20	3927.80	11.92	55	9.87
10	226.69	11.30	343040	ND	3.04	0.87	324.21	581.15	10561.00	10.86	7207.30	1.39	229.13	0.74	4509.80	4.08	130	ND
11	134.85	15.52	309640	ND	2.76	3.82	242.79	493.67	6745.30	7.37	6662.50	1.06	209.52	0.83	4523.10	1.90	100	ND
12	156.63	26.19	321910	ND	2.29	0.81	255.49	564.05	6794.80	7.89	7408.00	1.16	330.44	0.67	3815.70	2.60	110	8.44
13	141.10	18.69	330020	ND	1.85	1.09	277.96	675.65	7046.90	7.17	7798.00	1.22	216.48	0.56	4884.50	1.83	59	ND
14	88.80	21.25	313420	ND	2.25	0.64	157.08	604.92	5065.60	4.54	7832.00	0.89	261.85	0.62	4929.80	1.54	136	14.60
15	114.56	16.65	321110	ND	3.47	1.82	159.15	664.35	4812.70	4.24	7863.60	1.28	292.62	0.90	5344.00	1.73	37	6.62
16	202.29	23.72	316230	ND	2.31	1.84	361.47	615.49	5364.80	7.09	7534.90	1.34	209.49	1.03	4771.30	2.42	50	6.76
17	136.79	10.27	347840	ND	1.99	0.98	150.63	554.77	3804.10	3.37	7629.30	0.90	234.00	0.77	4372.10	2.25	55	9.60
18	115.74	11.75	340660	ND	2.28	0.71	151.68	532.70	3421.40	3.45	7158.40	0.92	235.20	0.36	4295.10	2.21	60	11.40
19	233.81	11.02	314060	ND	2.28	1.10	275.20	699.99	7917.20	9.13	7963.60	1.43	199.61	0.86	4134.50	3.03	50	ND
20	386.38	10.22	332730	ND	4.30	1.40	655.53	885.81	8362.10	13.79	8016.20	1.90	292.37	0.62	4533.50	5.07	43	9.27
21	261.02	11.15	317610	ND	4.50	1.03	744.69	581.49	6250.60	11.80	7581.20	1.67	289.94	0.89	3897.00	4.84	110	268.00
22	284.58	11.72	313610	ND	3.75	1.12	406.33	725.10	5736.60	10.97	8050.50	1.89	350.01	0.71	3938.80	2.40	110	189.00
23	278.76	15.03	329730	ND	3.47	1.22	522.35	928.81	7963.00	11.13	10676.00	1.86	407.71	0.79	3215.90	2.34	88	3648.00
24	201.11	37.29	323830	ND	3.24	6.21	355.61	938.78	6759.50	11.85	8545.00	4.32	317.91	1.13	4359.10	3.38	120	262.00
25	554.49	5.90	97394	ND	5.40	5.56	4873.20	261.71	2570.20	27.79	4685.40	3.40	641.39	3.67	1477.90	3.52	220	25.90
26	4980.60	47.96	54921	ND	184.92	184.24	44992.00	1427.00	3346.60	207.94	3254.00	49.68	717.52	129.53	591.37	26.30	1680	50.60
Average ± S.D	554.49 ± 4980.60	5.90 ± 47.96	304402.12 ± 68205.59		11.12 ± 35.55	8.76 ± 35.82	2361.30 ± 8745.42	692.75 ± 223.22	6257.93 ± 1917.02	18.55 ± 39.08	7551.58 ± 1366.88	3.62 ± 9.45	309.47 ± 121.32	5.95 ± 25.21	3916.41 ± 1019.10	4.46 ± 5.03	150.19 ± 315	284.17 ± 901.72

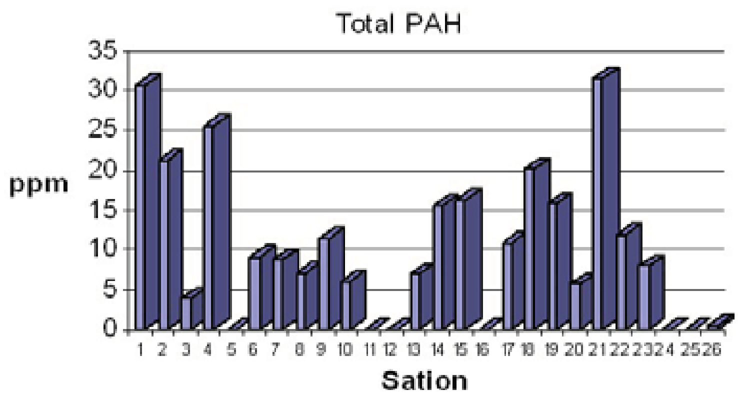


Fig. 12: PAHS variation in Zakum field.

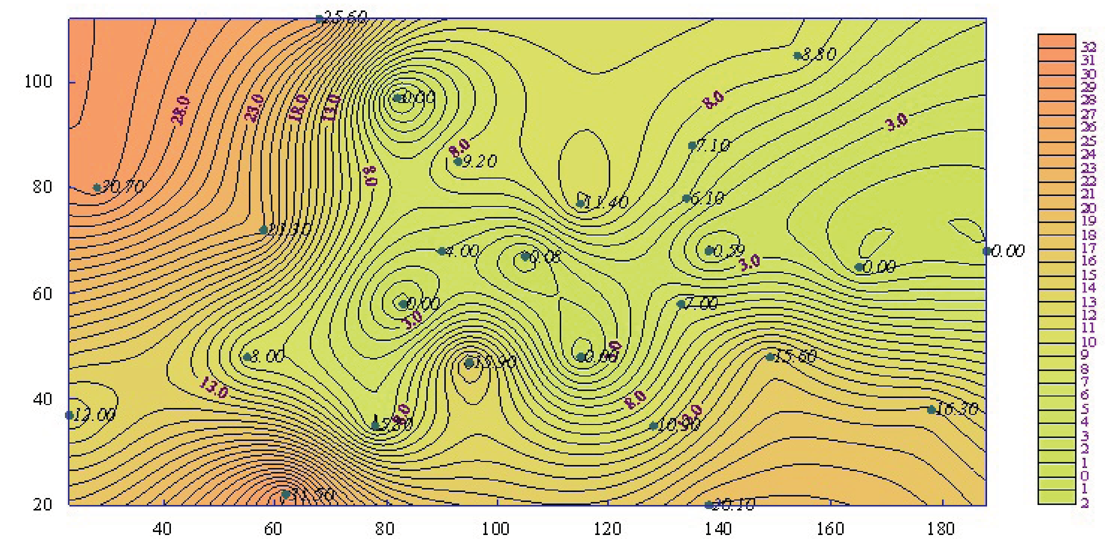


Fig. 13: PAHs contour map in Zakum field.

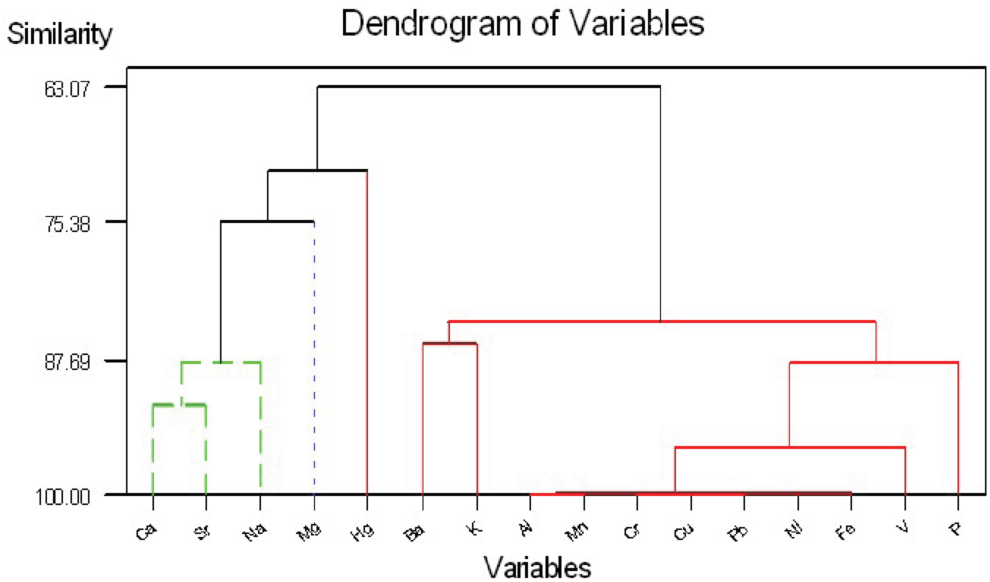


Fig. 14: Cluster Analysis of Heavy Metals Associations in the Bottom Sediments at Different Stations.

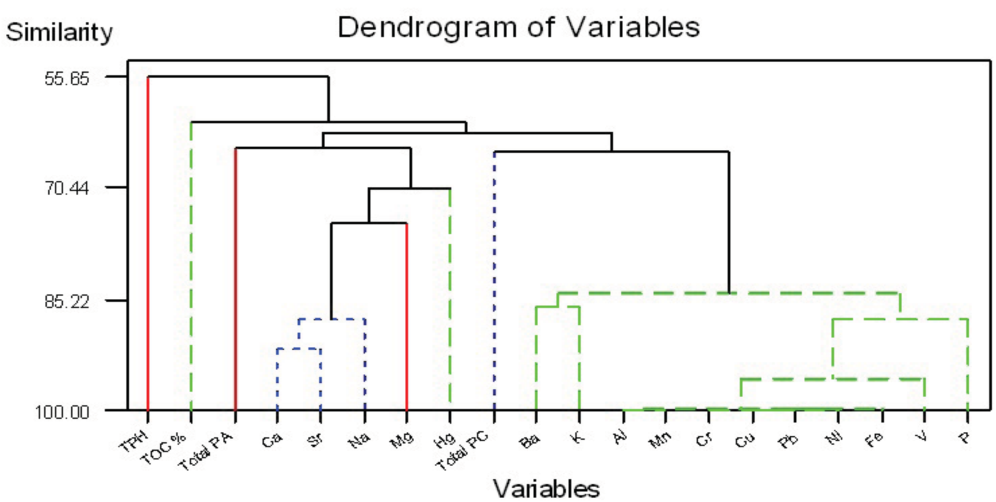


Fig. 15: Cluster Analysis of Heavy Metals, TPH, TOC%, Total PAH and Total PCBs Associations in the Bottom Sediments at Different Stations.

Distinguishing Biogenic Hydrocarbons from Petrogenic Hydrocarbons:

Characterization and differentiation of hydrocarbons from different sources is an essential part of any objective oil spill study. After oil spills, oil hydrocarbons often mix with other background hydrocarbon sources in the impacted area. One of the potential sources of hydrocarbons contributing to the background is biogenic hydrocarbons. Hydrocarbons from both anthropogenic and natural sources including biogenic source are very common in the marine and inland environments. Biogenic hydrocarbons are generated either by biological processes or in the early stages of diagnosis in recent marine sediments. Biological sources include land plants, phytoplankton, animals, bacteria, macroalgae and microalgae. The distinct characteristics of biogenic hydrocarbons including much higher abundance of odd n-alkanes in wide range of n- C21 to n- C33 and high CPI and pristane / phytane values. However, the presence of petrogenic hydrocarbons were also obvious, indicated by the distribution of n- alkanes in a wide range from C15 to C40 and the notable presence of the chromatographic UCM.

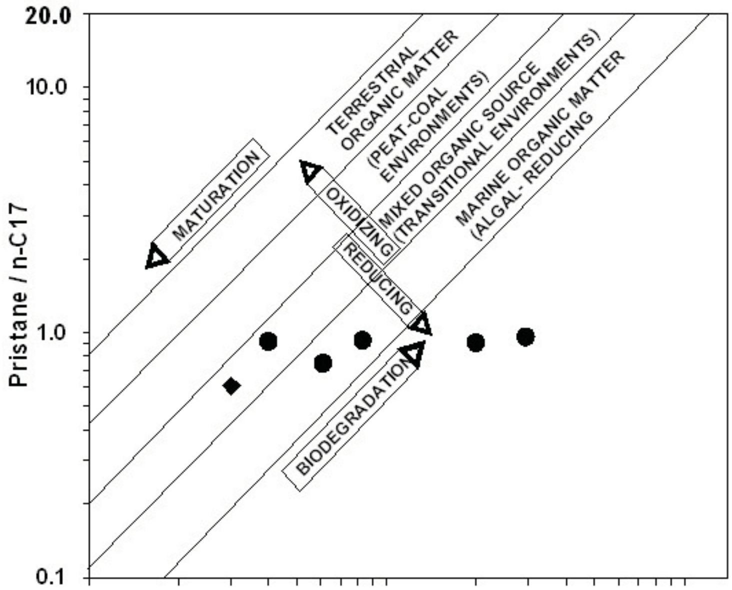
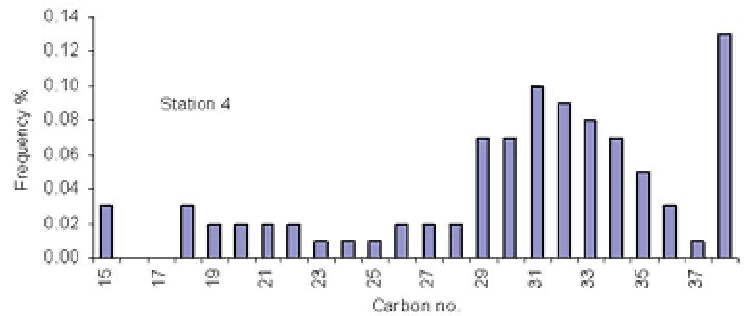


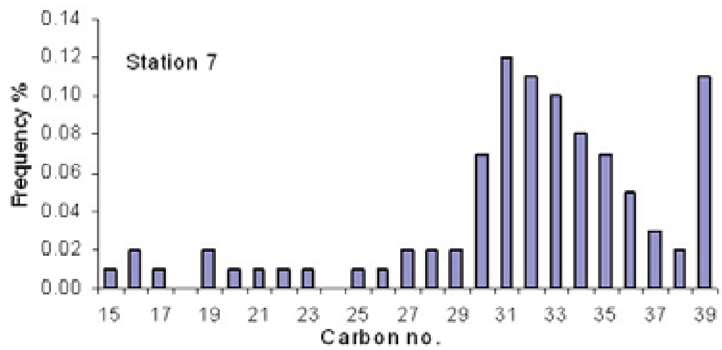
Fig. 16: Plotting of pristine/n-C17 versus phytane/n-C18 showing source type of the extracted hydrocarbons and oil in Zakum field (after shanmugam, 1985)

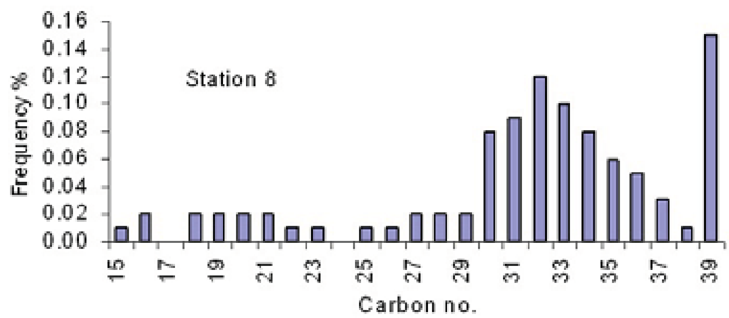
It has been recognized in the studied off shore sediments in Zakum field, UAE that the biogenic hydrocarbons have the following chemical composition characteristics: (1) n-alkanes show a distribution pattern of odd carbon – numbered alkanes being much abundant than even carbon – numbered alkanes in the range of n- C 21 to n- C33, resulting in unusually high carbon preference index (CPI) values, which is defined as the sum of the odd carbon – numbered alkanes to the sum of the even carbon – numbered alkanes (oils characteristically have CPI values around 1.0); (2) notable absence of the " unresolved complex mixture (UCM)" hump in the chromatograms; (3) pristine is often more abundant than phytane, suggesting a phytoplankton input and resulting in abnormally high pristane / phytane ratio values; (4) wide distribution of the biogenic PAH perylene, an unsubstituted PAH produced in subtidal sediments by a process known as early diagenesis. In the study of hydrocarbon biogeochemical setting of off shore sediments in Zakum field oil spill experimental site, we found that very high pristane / phytane ratios (0.38 to 1.59) and CPI values (0.45 to 1.16). High concentration of pristane relative to phytane in most off shore sediments indicate biological hydrocarbon input from a marine biological source (planktonic or bacterial) origin.

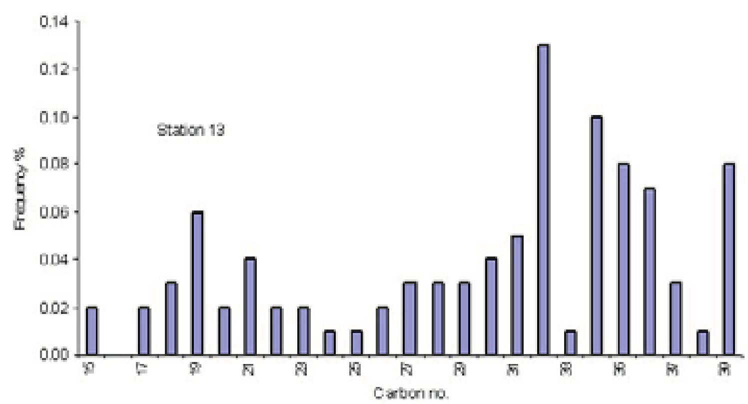
Oil Spill Identification:

In addition for measuring TPH in samples, GC – FID chromatograms provide a distribution pattern of petroleum hydrocarbons (e.g., carbon range and profile of UCM), fingerprints of the major oil components (e.g., individual resolved n-alkanes and major isoprenoids), and information on the weathering extent of the spilled oil. Comparing biodegradation indicators (such as pristane / n – C17 and phytane / n – C18) for the spilled oil with the source oil Fig. 16 can be also used to monitor the effect of microbial degradation on the loss of hydrocarbons at the spill site. Crude oil compositions vary widely. Depending on the sources of carbon from which the oils are generated and the geologic environment in which they migrated and from which reservoir, they can have dramatically varied compositions in C5 to C40 carbon range such as relative amounts of paraffinic and asphaltenic compounds, large differences in the n-alkane distribution and UCM, and significantly different relative ratios of isoprenoids to normal alkanes Zhendi Wang (2000). Fig. 17 shows GC-FID chromatogram for two different oils. Clearly, these two oils are very similar, there large similarity in the n-alkane distribution and UCMs, as well as in relative ratios of isoprenoids to normal alkanes. The ratios of pristane / n-C-17and phytane/ n-C-18 have been found to be virtually altered from those measured for bottom sediments.


Station 4
Frequency %
Carbon no.


Station 7
Frequency %
Carbon no.


Station 8
Frequency %
Carbon no.


Station 13
Frequency %
Carbon no.

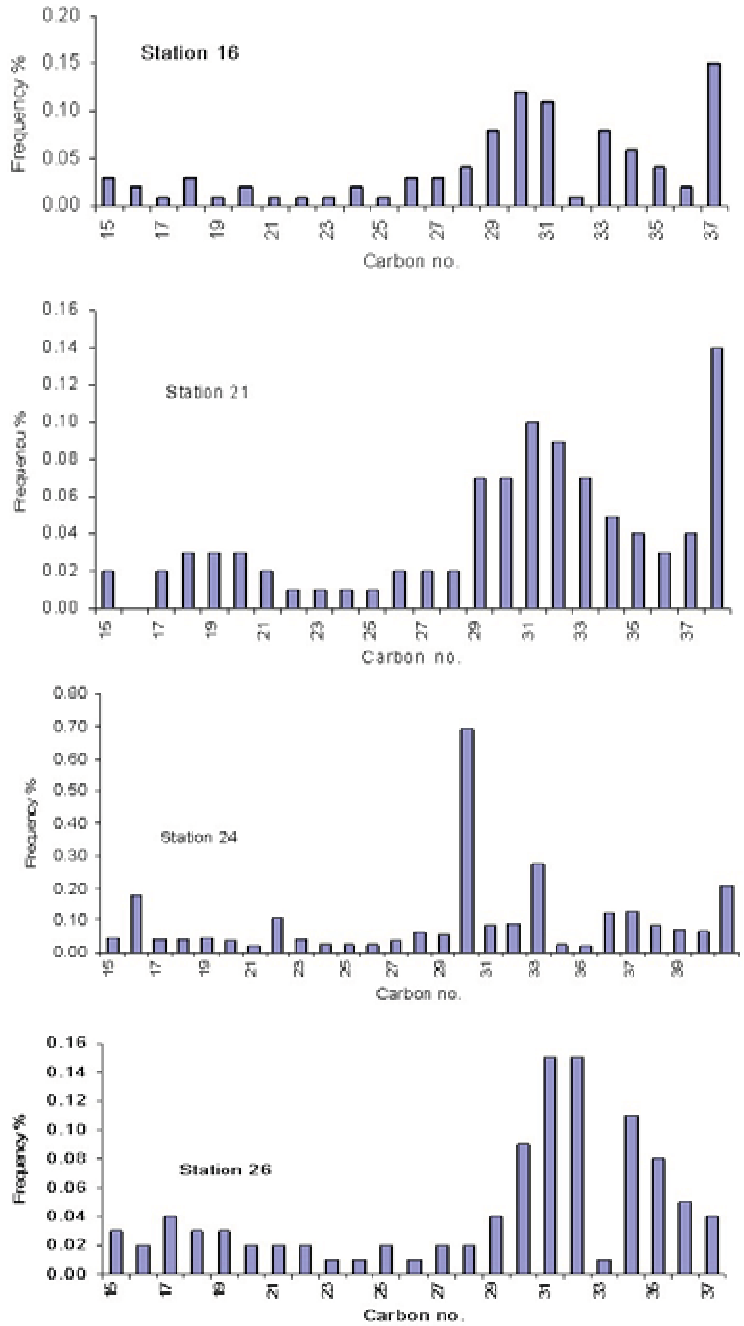


Fig. 17: The relation between carbon number and the frequency % of the extracted hydrocarbons and oil of Zakum field

Conclusions: This review focuses on recent applications of various advanced chemical fingerprinting and data interpretation techniques for the source identification of spilled oils. The techniques discussed include oil – characteristics hydrocarbon distribution pattern recognition. The issues on distinguishing biogenic and pyrogenic hydrocarbons from petrogenic hydrocarbons are also discussed. In many cases, however, particularly for complex hydrocarbon mixtures or extensively weathered and degraded oil residues, there is no single technique which can unambiguously identify the source(s) of unknown spills and qualitatively allocate hydrocarbons to their respective sources. The comprehensive chemical data from analysis of off shore sediments in Zakum field, UAE indicate the following:

- TOC increases from 0.33 wt% to 14.96 wt% towards the northern sector of the field area.
- TKN ranges from 13.4 mg% to 136 mg% with a marked increase in the central part of the field area.
- TPH is increasing from 6.14 ppm to 62.7 ppm towards the northern part of the field area which could be classified as slightly polluted area.
- Association of the high TPH and TOC values to the lithogenic metals rather than man-made confirms the biogenic origin for the hydrocarbons.
- ∑PAHs is ranging from below detection level to 31.5 ppm with an increasing trend towards the northwestern parts of the field area.
- The off shore sediments in Zakum field, UAE can be categorized into one group.
- The biogenic cluster was obvious and no UCM was observed.
- It has been recognized that hydrocarbons from natural sources including biogenic source are very common in the marine and inland environments.
- The offshore sediments showed typical biogenic n-alkane distribution ranging form C21 to C33 with abundance of odd-carbon number n-alkanes being much higher than that of even-carbon number n-alkanes.
- Only station 25 in the central part was sourced from petrogenic hydrocarbons as clearly indicated in the GC chromatograms.
- Most of heavy metals show normal distribution curve in the bottom sediments. Heavy metals associated with hydrocarbon pollution (Cu, Ni, Pb, V, Cr) display hi concentrations in stations 3, 5, 9 and 26.
- Hg is only detected in the central sector of the field area.
- Monitoring should be conducted for the northern and central sectors of the field area particularly at station 26 as it attains the highest values of the pollution parameters.
- Monitoring is recommended for the western and southern sectors to document changes in the PAHs and PCBs concentrations.

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