LJAST
Libyan Journal of Applied Science and Technology
مجلة ليبيا للعلوم التطبيقية والتقنية

Volume 13 Issue 02
December 2025
ISSN 2958-6119

مجلة ليبيا للعلوم التطبيقية والتقنية

Comparison of Petroleum Hydrocarbon Levels in Western Libyan Beach by Gravimetric and Spectroscopy Analysis

Ali. A. Ejbali, Dr. Elmabruk H. Ali, Muhsen J. Ghurbaj, Najwa A. Shames
Chemical and Environmental Engineering Department
Engineering Technology College, Tripoli, Libya.

ABSTRACT

Fourteen shore water samples (denoted as w) from west of Tripoli shoreline, were examined for their petroleum hydrocarbon contents by gravimetric and spectroscopy analysis.

Known amounts of beach water (w) were extracted with a suitable volume of chloroform ($CHCl_3$). The extracts were measured spectrophotometrically through calibration curves of absorptions at 410nm and 260nm to determine the concentration of petroleum hydrocarbons.

Infrared analysis was also conducted on hydrocarbons extracted from shore water samples to assess the degree of oxidation occurred to extracted hydrocarbons. This was obtained by comparing the relative absorption values at 1736 and 1712cm^{-1} , normalized with respect to 2925 cm^{-1}; C-H stretching vibration; to rule out effects due to concentration.

Gravimetrically, hydrocarbon concentrations in shore water (w) ranged from 0.05 to 9.50 ppm, while spectrophotometrically concentrations at 260nm and 410nm ranged from 0.470 to 2.74ppm, depending on location and industrial activities. The variation between the hydrocarbon concentrations by gravimetric method and spectrophotometric method was due to the fact that gravimetric method measures total organics, but spectrophotometric method focused on hydrocarbons which is a subset of organics. The Infra-red analysis showed densities at 1736cm-1 (Acid-I) and 1712cm-1 (Acid-II) which normalized with respect to the absorbance at 2925cm-1 (Alkyl C-H) being equal to 1.00, the results were ranged 0.044 to 0.128 as acid-I and ranged 0.027 to 0.088 as acid-II, depending on effects of Prevailing Conditions.

Keywords: Western Libyan Beach, Petroleum, Hydrocarbon Levels, analysis, gravimetric method

1- INTRODUCTION

Periodical measurements on the concentration of hydrocarbons polluting sea water are of great relevance to a country like Libya with shores extending near two thousand kilometers. We believe this practice is of extreme importance since more than 80% of population and industries, including all petroleum refining and exporting operations; are located on the shore and the existence of offshore petroleum operations and activities (e.g. Bouri-Petroleum field). In addition, the sea we are dealing with is the Mediterranean Sea which is considered the busiest sea transport lines serving North Africa and European countries.

Geographically the Mediterranean Sea is nearly a lake being connected with the Atlantic Ocean through Gibraltar Straight, which is of ~21-kilometer width only. Concern on the importance of sea water near the Libyan shores was initiated previous report on marine pollution studies on petroleum hydrocarbon levels near El- Bouri Field (1988), [Ref. 1].

Part of the map of Libya concerned, about 200km shoreline is given in Fig.-1

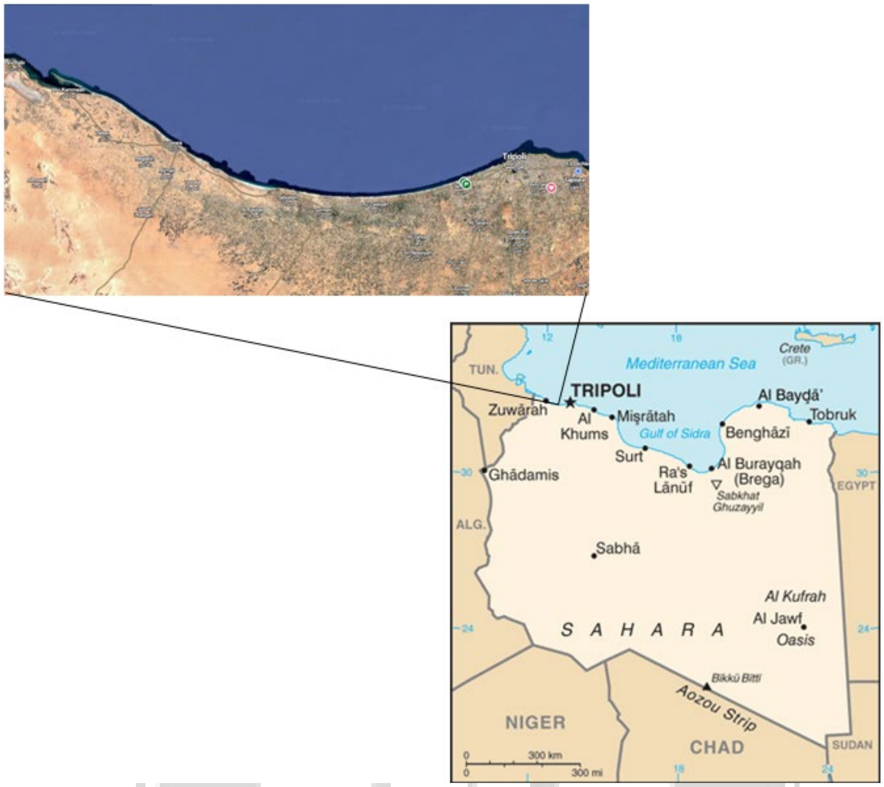


Fig. -1: Map of West Tripoli Shoreline

The results in this paper will be used as a base for comparison within western of Tripoli zones. This paper was designed to focus on the following objectives:

1. Determination and comparison of petroleum hydrocarbon concentrations, with some understanding of their nature and chemical alterations, affected by prevailing conditions.
2. Development of reliable and fast methods of chemical measurements.

There is ample evidence documented in literature regarding toxic effects of petroleum hydrocarbons on marine life, and in turn on human health [2,3]. Several published papers and United Nations report on the concentration of hydrocarbons in the Mediterranean Sea are available [,4,5,6,7,8]. Libyan concern on the subject is reflected in the reports of Marine Fisheries Research Centre [10] and Petroleum Research Centre reports and publications [9].

In this part, the concentration of petroleum hydrocarbons was investigated in collected water and in shore sand (dry and wet) with an attempted correlation with human activities in each sampling station. Chemical changes induced by weather parameters are also investigated by spectrophotometric techniques.

2- EXPERIMENTAL :

1: Extraction and Gravimetric Determination of Hydrocarbon in w:

250 ml of sea water was extracted with chloroform (3×50ml) in a separatory funnel. Extracts were combined and dried with 20g of anhydrous Na_2SO_4. The mixture was Shaked and was left to stand (sealed), overnight. Next day most of $CHCl_3$ solvent was decanted in a pre-dried and weighed distilling flask. Na_2SO_4 layer was washed with 30ml of dry* $CHCl_3$ and was filtered. Filtrate and decantated were combined and $CHCl_3$ was distilled in a rotavapour equipment under mild conditions (~60°C and 0.5bar pressure). Residual matter was dried 1h in an oven at 105°C and concentration of extracted hydrocarbons was calculated.

[(*) 200ml of CHCl3 was dried by adding to it 50g anhydrous Na_2SO_4 and was kept overnight, followed by decantation.]

2: Calibration curves for UV-Vis Spectrophotometric Determination of Hydrocarbon Concentration in sand and water samples:

(1) 42.2 mg of a blend of hydrocarbons extracted from water according to procedures 1 above was first dissolved in 25ml of dry $CHCl_3$ to give the Base-Stock (BS) solution containing $1.68 mg.ml^{-1}$ of hydrocarbon.

(2) Portions of this BS solution were diluted in 25ml each of dry $CHCl_3$ to give new solutions as described in the following table.

Solution No.	BS.ml/25mlCHCl3	Conc. of Hydrocarbons ($mg.ml^{-1}$)
1	0.5	0.034
2	1.0	0.067
3	1.5	0.101
4	2.0	0.134
5	2.5	0.168
6	3.0	0.202

3: Procedure for Spectrophotometric Determination of Hydrocarbons in Water Samples (w):

A volume of 250ml of sea water was extracted with 3×50ml portions of reagent grade $CHCl_3$ in a separatory funnel. The extracts were combined then volume of $CHCl_3$ was reduced to about 20ml by distillation under atmospheric pressure. The extract was transferred to a 25ml vol. flask, and the volume was made up to the mark by adding few mls of $CHCl_3$. UV-VIS absorbencies at 260 and 410nm were measured. The hydrocarbons concentration in sea water in µg/l were calculated with the aid of the calibration curves taking into accounts volume reduction.

4: Infra-red Measurements on Separated Hydrocarbons:

Few milligrams of hydrocarbons separated in 1 above were dissolved in 0.5ml spectroscopic grade CCl_4 and IR was obtained against CCl_4 in the reference cell. Absorption regions of interest: 2800-3000cm^{-1} and 1700-1750cm^{-1} were measured.

5: Other Experimental Details:

- Water samples were brought in clean, dry and dark glass bottles which were tightly sealed after sampling and were processed as fast as possible.

- UV-Vis Spectrophotometer used was PU 8800 Double Beam.

- IR. spectrophotometer used was PYE UNICAM PU 9512.

Spectra were obtained in CCl4 solutions.

- Chloroform used in this work supplied by Fluka Chemicals and was used assuch or dried when necessary.

3- RESULTS:

The exact location of sampling sites with proper abbreviations used are given in Table-1.

Table-1: Sampling Locations and Abbreviations

Abbrevi-ation	Site Description	Abbrevi-ation	Site Description
BKM	Abuo-Kammash	MRC	Marine Research Center.
ZWA	Zuwarah	PS	Power Station

SBR	Sabratah	w	Water
ZAW	Zawiyah	W	West
TRIP	Tripoli	E	East
TAJ	Tajorah	Km	Kilometer.
REF	Refinery	UV	Ultraviolet
HARB	Harbour.	VIS	Visible
JAZ	Janzour	R.O.C.	relative oxidized carbon

3- 1 Gravametric Measurements:

Table-2 gives the average results on the extractions of hydrocarbons by chloroform from water (w). Fig. 2 represents these gravimetric results graphically.

Table-2: Average Gravimetric Determination of hydrocarbons Extracted by Chloroform.

Sampling Site	Chloroform Soluble Hydrocarbons (ppm)
2Km/W-BKM	1.5
BKM	4.5
2Km/E-BKM	3.1
7Km/W-ZWA	3.9
1Km/W-ZWA	-
2Km/E-ZWA	-
SBR	1.3
7Km/W-ZAW-REF	-
3Km/W-ZAW-REF	-
ZAW-REF-HARB	9.7
1Km/E-TRIP-PS	-

DF	0.05
MRC	0.05
TAJ	-

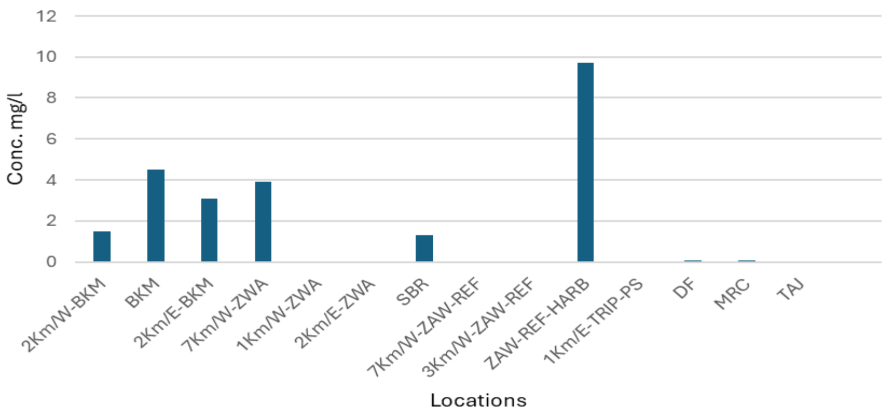


Figure -2 : Gravimetric determination of hydrocarbons in water (w) by CHCl3 extraction

3- 2 Spectroscopic Measurements:

Due to several errors expected when applying gravimetric method to extraction of highly diluted solutions of materials. This prompted us to use more accurate, and rapid alternative methods for determining hydrocarbon concentrations, especially in sea water. A standardized UV-VIS spectra of hydrocarbon extracts measured in different concentrations in chloroform are shown in figure-3. Table-3 gives corresponding standardized absorbance values at 260 and 410nm. The calibration curves were used to calculate the concentration of hydrocarbons in the $CHCl_3$ extract directly after extraction, taking into accounts the volume of the original samples and the volume of extracts. The results are given in Table-4 and illustrated in figure 4.

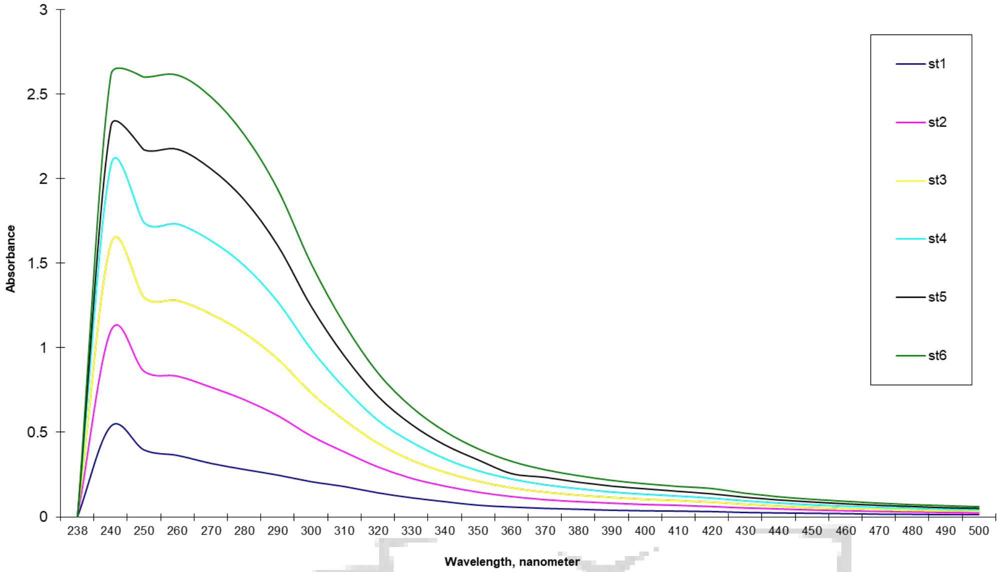


Figure-3 UV-VIS Spectra of Hydrocarbon Extracts Measured in Different Concentrations in Chloroform

Table - 3: Standardized concentrations and UV-VIS absorbance of hydrocarbons extracted by $CHCl_3$

Sample No.	Standardized con. mg/ml	UV-VIS Absorbances	
		λ_{260} nm	λ_{410} nm
1	0.033	0.395	0.034
2	0.067	0.859	0.068
3	0.101	1.299	0.097
4	0.134	1.740	0.123
5	0.168	2.170	0.151

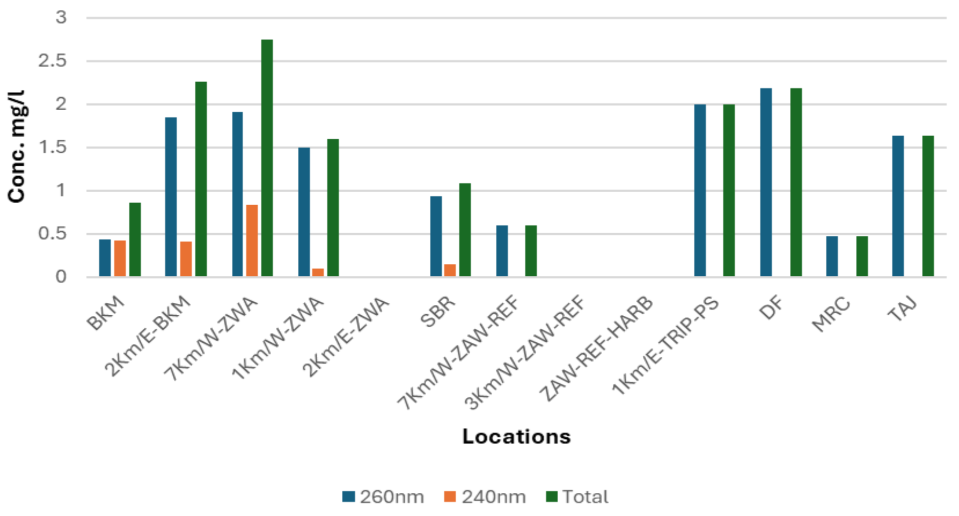
6	0.202	2.603	0.180

Table-4: Average UV-VIS Spectrophotometric Results of Hydrocarbons in Water Samples Extracted by Chloroform

Sampling site	**Hydrocarbon Conc. (ppm)**		
	260nm	**410nm**	**Total**
BKM	0.430	0.428	0.858
2Km/E-BKM	1.850	0.412	2.262
7Km/W-ZWA	1.910	0.830	2.74
1Km/W-ZWA	1.500	0.098	1.598
2Km/E-ZWA	n.d.	n.d.	n.d.
SBR	0.940	0.150	1.09
7Km/W-ZAW-REF	0.594	n.d.	0.594
3Km/W-ZAW-REF	n.d.	n.d.	n.d.
ZAW-REF-HARB	n.d.	n.d.	n.d.
1Km/E-TRIP-PS	1.990	n.d.	1.99
DF	2.178	n.d.	2.178
MRC	0.470	n.d.	0.47
TAJ	1.630	n.d.	1.630

n.d. = not detected.

Fig. 4 Average UV-VIS Spectrophotometric Results of Hydrocarbons in Water Samples Extracted by Chloroform



Limited qualitative investigation on hydrocarbons in water (w) samples was conducted through infrared (IR) measurements. Figure-5 gives the changes in the IR absorptions pattern in the range 1500 to 3500 cm^{-1}, measured in CCl_4 solutions, where:

a- Typical crude oil (Sedra).

b- Hydrocarbons extracted from shore water (w).

In order to make measurements independent of dilution, relevant optical densities at 1736cm^{-1} (Acid-I) and 1712cm^{-1} (Acid-II) were normalized with respect to the absorbance at 2925cm^{-1} (Alkyl C-H) being equal to 1.00, in each measured sample. The results are given in Table-5.

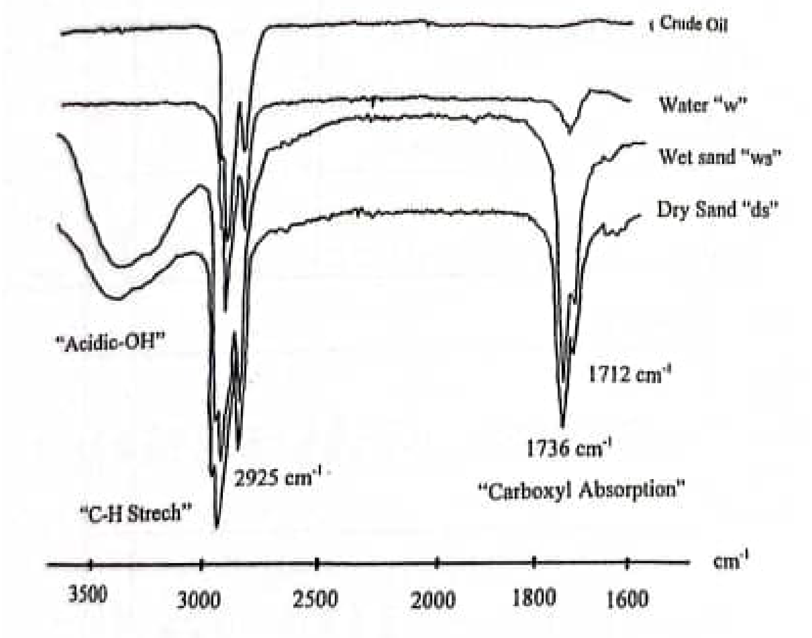


Fig.5: IR Absorption Pattern at 1500 to 3500 cm-1, Measured in CCl4

Table 5: Normalized IR Measurements With Respect to A2925cm^{-1} = 1.00

Sample No.	**IR Absorbances**	
	Acid-I	**Acid-II**
2Km/W-BKM	-	-
BKM	-	-
2Km/E-BKM	0.044	-
7Km/W-ZWA	0.090	0.088
1Km/W-ZWA	-	-
2Km/E-ZWA	0.095	0.027
SBR	0.128	-
7Km/W-ZAW-REF	-	-
	-	-

3Km/W-ZAW-REF	-	-
ZAW-REF-HARB	-	-
1Km/E-TRIP-PS	-	-
DF	-	-
MRC		
TAJ		

4- DISCUSSION AND CONCLUSSION

Pollution of near shore sea water with petroleum hydrocarbons is a dynamic system affected by several natural phenomena and anthropogenic activities such as:

1. Prevailing wind direction, sea currents and waves push floating oily matter to shore.
2. Sinking of oily matter to bottom by natural phenomena such as sandstorms or by intentional addition of materials to enhance the sinking operation to prevent shore contamination, increases pollution of the bottom sand.
3. Sunken oily matter may float after a while (e.g. when weather conditions are changed, or as a result of some biological effects; thus, increasing surface water pollution hazards.
4. Organic deposits on the near shore sand coming from variable sources; which are mostly anthropogenic; may wash down to sea after heavy rain falls.
5. Organic waste on land and in the sea (floating or sunken) may suffer noticeable chemical changes due to atmospheric oxidation and biological alteration through digestion by aerobic and anaerobic microorganisms.

In this paper the focus was on shore water. Emphasis was made first on the methods for determining the concentration of hydrocarbons. The second point of interest was throwing light on the chemical nature and some of the chemical changes suffered by these hydrocarbons as a consequence of prevailing conditions.

4-1 : Methods for Concentration Determination:

Chloroform was chosen as a solvent for extracting the hydrocarbons since it is quite suitable for the sort of study we intend to carry out and it′s successful use is very well documented in published literature. The extraction operation was conducted in duplicate runs in most cases of water samples. Full details of extraction results are given in Table-2 and plotted in Figure-2.

The main observations from these results are the following.

1. Concentration in water samples is considered low.
2. Gravimetrically, the noticeably high concentration in water samples in the vicinity Zawiyah refinery, 9.7ppm followed by Aboukamash area, 4.5ppm.
3. Anthropogenically intervention through industrial activity may account for the very high values of 9.5ppm west Zawiyah refinery.

The gravimetric method of chloroform extraction involves several steps of weighing, extraction, drying of solution, drying of extract and the possibility of hydrocarbons dissolution in $CHCl_3$. Possible sources of error will be reduced by reducing human intervention.

Most petroleum organic structures possess(c=c) aromatic bonding absorbing in the UV range of 250-260nm. Other constituents; especially those of large molecules; may absorb visible light in the range 410-420 nm thus appearing yellowish in their diluted solutions. The aromatic structures in the latter large molecules usually absorb UV-light at higher wavelengths than 260nm (usually 260-280nm), thus a spectroscopic method is mostly specific. Further to this, it involves less steps, once a calibration curve is set. The result on hydrocarbons concentrations in water (w) by the spectrophotometric method, using the calibration curves, are given in Table-4.

The main observations from these results are the following:

1. The concentration of hydrocarbons at UV spectrum (λ_{260}) and VIS spectrum (λ_{410}) in water samples (w), can be measured by the spectroscopic method approaches, which affords further information on the real nature of hydrocarbons.
2. It is believed that the spectroscopic method is more accurate, and there is reasonable explanation that the λ_{260}, low molecular weight hydrocarbons and larger molecular weight hydrocarbons at λ_{410} are distinguishable which cannot be obtained by gravimetric method.

infrared (IR) spectroscopic measurement showed partial oxidation by atmospheric oxygen to carboxylic acids [11,12,13]. Figure-5 clearly shows the formation of carboxylic absorptions at 1736 and 1712cm-1 and acid hydroxyl absorption at 2500-3500cm-1 due to the Exposure of hydrocarbons of petroleum origin to ambient atmospheric conditions.

REFERENCE

1- "Marine Pollution Studies on Petroleum Hdrocarbon levels Near El-Bouri Field" PRC Reports (1988).

2- Neff, J. M. , and Anderson, J. W. (1981), Applied Science Publishers Ltd. London.

3- Geyer, R. A. , (1980), Elsevir Scientific Publishing Company, Amsterdam.

4- International Oceanographic Commission, World Meteorological Organization, United Nations Environmental Programme, Coordinated Mediterranean Pollution Monitoring and Research Programme (IOC/WMO/UNEP/MEO-MRP/3 Supp.2), Paris (1977).

5- International Juridical Organization (I.J.O.), UNEP/WG36/5(1979)

6- Zsolnay, A. , Marine Chem. (1979), 7, 343.

7- UNEP, Tech. Rep. 7 (1986).

8- UNEP/WG/11 (1987).

9- Marine Fisheries Research Centre, (1981) Libyan Bull. No.1.

10- Ali, L. H. , Al-Jawashi, S. , El-Jelani, S. (1995). "Conf. on New Technologies Applied to Hydrocarbon Production". Sept. 12-15, Delft, the Netherlands.

11- " Soil and Water Pollution by Spent Lubricating Oil", Ali, L. H. , etal. (1979). Environment International, Vol. 2, 61.

12- "Water Pollution by Spilled Crude Oil", Ali, L. H. , etal (1987). Proceeding, World Symp. on Environ. Pollution Management. Istanbul, Turkey (PP 79-96).

13- "Water Pollution by Petroleum and Its Derivatives", Ali, L. H. , etal (1985). Proceeding, Regional Conference on Enviro. Pollut. Abatement, May 13-16, Habbaniya, Iraq.