# Studies on River Nile Aquatic Environment II. Organic Pollutants

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**Abstract:** This study has been carried out on river Nile water and sediment samples to investigate the organic contaminants present. Oils were extracted gravimetrically from the studied samples to determine the oil content and analyzed by gas chromatography to determine n-, iso- paraffins and unresolved complex molecules (mainly aromatic and naphthenic), by high performance liquid chromatography to determine polyaromatics and by infrared spectrometry for the determination of the different functional groups. Data analyses indicate that the environmental hydrocarbons pollution comes from middle petroleum distillate fractions used in shipping activities.

**Key words:** Water analysis · Organic pollutants · N-paraffins · Gas chromatography · Polyaromatics · High performance liquid chromatography and infrared spectrometry

## INTRODUCTION

River Nile is one of the most important rivers in the world. It is the main resource of water in Egypt that has a wide usage in different fields, drinking and domestic water supply, agricultural, industrial, navigation, fishery and others. Therefore "Egypt is the Gift of the Nile" this is what Herodotus meant Egypt depends entirely in its agriculture which in turn accounted as the real beginning of the rise history of civilization on River Nile banks that supports the life of Egypt across long ages [1]. Six surface water samples from River Nile were collected at Manyal, Zamalek and Agouza (Cairo); two from each, one from the near shore and the other 10 m apart and one sample from Esna.

**Experimental**
**Determination of Organic Pollutants:** Organic pollutants of water and sediment samples were analyzed as follows:

- Extraction of oils from the water samples by carbon tetrachloride,
- Extraction of oils from sediment samples by n-pentane.
- ractionation of the extracted oils by gas chromatography to determine n- paraffins (n-P), iso-paraffins (iso-P) and unresolved complex molecules (UCM)

- Fractionation of the extracted oils by high performance liquid chromatography to etermine polyaromatics and
- etermination of functional groups of the extracted oils by infrared spectrometry.

**Extraction of Oils from the Water Samples by Carbon Tetrachloride:** Extraction of the oils from the water samples was performed and determined by the gravimetric method according to the ASTM D 4281 and APHA 5520 B standard methods [2, 3].

**Procedure:** One litre of the water sample was acidified by HCl solution to pH < 2 and poured into a separating funnel, then extracted with 30 ml carbon tetra chloride as a solvent for 15 min. Solid NaCl was added to water samples that form emulsions to enhance solvent separation. The solvent layer was drained through a filter paper moistened with the solvent and contained anhydrous sodium sulphate. The extracting step was repeated twice more. The extracts were combined in a clean, dry weighing flask and the filter paper was washed with 10-20 ml of the solvent. The extracted oil was dried in an oven at 76°C, cooled in a desiccator to constant weight.

**Extraction of Oils from Sediment Samples:** Three sediment samples from Nile River were collected at Manyal, Zamalek (Cairo) and Esna. Oils in the studied

sediment samples have been extracted according to Viguri *et al.* [4].

**Procedure:** To 100 g of dry sediment in a round bottomed flask, 100 ml redistilled methanol and 3 g potassium hydroxide were added. The mixture was refluxed for 1.5 hours. The saponified extract was cooled, transferred to a separating funnel, then extracted with 25 ml n-pentane as a solvent for 15 min. The extract was dried through a column packed with anhydrous sodium sulphate. The extracting step was repeated twice more. The extracts were combined in a clean, dry weighing flask. The extracted oils were dried in an oven at 50°C, cooled in a desiccator to constant weight and finally the oil content was calculated.

**Determination of *n*-, iso- Paraffins by Gas Chromatography:** The extracted oil from each studied water or sediment sample was analyzed by gas chromatography to determine n-, iso- paraffins and unresolved complex hydrocarbons.

**Apparatus Used:** A gas chromatograph, model Agilent 6890 plus, equipped with a flame ionization detector, a fused silica (HP-1) capillary column (30 m x 250 μm), packed with poly(dimethylsiloxane) as stationary phase and an integrated data handling system.

**Procedure:** 1μl of oil solution dissolved in methylene chloride was injected into the injector heated at 300°C. The column temperature was programmed from 100 to 320°C at ramp rate of 3°C/min and nitrogen was used as a carrier gas with a flow rate of 2 ml / min. Retention times and areas of separated peaks in the chromatograms were determined by comparison with those of a reference sample of *n*-paraffins.

**Determination of Polyaromatics by High Performanc Liquid Chromatography:** Polyaromatics in the extracted oil were determined by high performance liquid chromatography (HPLC) according to the ASTM D 4657 standard method [2].

**Apparatus Used:** A HPLC machine, model Waters 600E, equipped with an autosampler Waters 717 plus, a dual wavelength absorbance detector Waters 2487 set at 254 nm and a column of Supelcosil LC-PAH, 15 x 4.6 mm ID, 5 μm particles size.

**Procedure:** 1μl of the oil dissolved in acetonitrile was injected into the column and a gradient elution was carried out with an acetonitrile-water (HPLC grades) mixture from 50: 50 to 100: 0, with a flow rate of 0.2 ml /min for the first 2 min, then 1.0 ml /min for other 43 min. The retention times and areas of the resulting peaks were recorded. A reference sample of polyaromatics (Supelco) was injected under the same conditions. The retention times and areas of its peaks were used to determine, qualitatively and quantitavely, each polyaromatic in the sample.

**Determination of Functional Groups of the Extracted Oils by Infrared Absorption Spectrometry:** Infrared spectra of the extracted oils were carried out using a FT-IR Spectrometer, model 960M000g, ATI Mattson Infinity Series. The infrared spectra of the oils were measured in the range of 4000-400 / cm using the KBr disc technique.

## RESULTS AND DISCUSSION

### A. Water Samples

**Organic Pollutants:** Oils in the studied water samples have been extracted with carbon tetrachloride using gravimetric method, the obtained results are given in Table 1, which indicate that the concentrations vary from 46.2 ppm to 174.3 ppm for near shore surface water having the following trend $1 > 3 > 2$; and from 22.1ppm to 52.9 ppm 10 m apart from shore having the trend $3 > 1 > 2$, while oil content is 456.4 ppm at Esna.

Excluding the amounts of n-$C_{25}$ (of biogenic origin), oil content ranges only from 14.9 ppm to 41.4 ppm for near shore surface water and from 4.83 ppm to 13 ppm 10 m apart from shore, whereby in Esna it is 88.99 ppm. The relatively higher concentrations in the near shore samples in sites 1 and 2 may be due to the tourstic ships landing there.

**Determination of *n*-, iso- Paraffins by Gas Chromatography:** The extracted oils from the studied water samples were analyzed by gas chromatography to determine the nature, type and source or sources of such pollutants.

The chromatograms obtained Fig. 1 show a series of n-paraffins peaks super imposed over a hump comprising of unresolved complex mixture mainly of aromatic and naphthenic compounds. The different isomers of the n- paraffins appear as small peaks in-between each two n- ones and n-$C_{25}$ appears as a highly predominant peak.

Table 1: Gas Chromatographic Analysis of the Extracted Oils from Water Samples

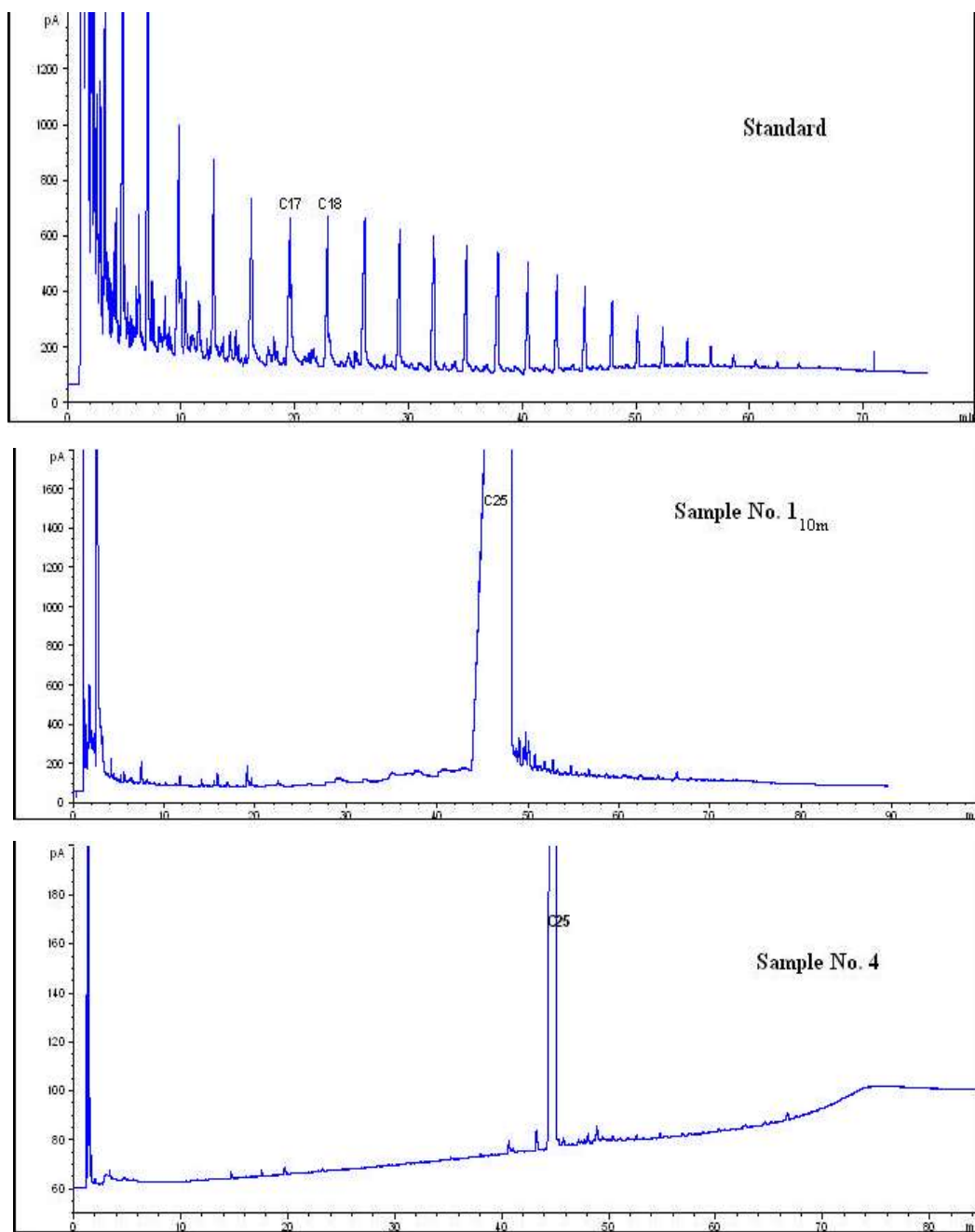| | Water Sample No. | | | | | | |
|---|---|---|---|---|---|---|---|
| Concentration | Manyal 1 | Manyal $1_{10m}$ | Zamalek 2 | Zamalek $2_{10m}$ | Agouza 3 | Agouza $3_{10m}$ | Esna 4 |
| Oil content ppm | 174.5 | 29.3 | 46.2 | 22.1 | 65.9 | 52.9 | 456.4 |
| Oil content- $n$-$C_{25}$ | 41.4 | 4.83 | 14.9 | 5.3 | 16.8 | 13 | 88.99 |
| $n$-$C_{13}$ | - | - | 0.0200 | 0.0267 | - | 0.0882 | 0.0345 |
| $n$-$C_{14}$ | 0.0230 | 0.0408 | 0.0263 | 0.0300 | 0.0413 | 0.5800 | 0.269 |
| $n$-$C_{15}$ | 0.0174 | 0.0354 | 0.0275 | 0.0235 | 0.0306 | 0.0246 | 0.0163 |
| $n$-$C_{16}$ | 0.0427 | 0.0565 | 0.0890 | 0.2362 | 0.0386 | 0.1904 | 0.09 |
| $n$-$C_{17}$ | 0.0498 | 0.0262 | 0.1695 | 0.0133 | 0.021 | 0.0156 | 0.0181 |
| $n$-$C_{18}$ | 0.0532 | - | 0.1823 | 0.0132 | 0.0154 | 0.0298 | 0.0249 |
| $n$-$C_{19}$ | 0.0650 | 0.0125 | 0.1922 | 0.0148 | 0.024 | 0.4568 | 0.2863 |
| $n$-$C_{20}$ | 0.0864 | 0.0113 | 0.1838 | 0.0164 | 0.0301 | 0.0735 | 0.0574 |
| $n$-$C_{21}$ | 0.1551 | 0.0172 | 0.2216 | 0.0442 | 0.0538 | 0.3203 | 0.0082 |
| $n$-$C_{22}$ | 0.2616 | 0.0212 | 0.2021 | 0.1004 | 0.0712 | 0.1078 | 0.1021 |
| $n$-$C_{23}$ | 0.3734 | 0.1163 | 0.2666 | 0.2356 | 0.0069 | 0.2756 | 0.0642 |
| $n$-$C_{24}$ | 0.4731 | 0.1992 | 0.2924 | 0.2949 | 0.2564 | 0.2987 | 0.0242 |
| $n$-$C_{25}$ | 76.2954 | 83.4789 | 69.5254 | 77.1532 | 74.5712 | 75.4311 | 80.4839 |
| $n$-$C_{26}$ | 0.1294 | 0.1024 | 0.1186 | 0.2396 | 0.1175 | 0.2974 | 0.2844 |
| $n$-$C_{27}$ | 0.5670 | 0.0409 | 0.0791 | 0.2391 | 0.20 | 0.2476 | 0.1175 |
| $n$-$C_{28}$ | 0.1697 | 0.0384 | - | 0.1748 | 0.0705 | 0.1581 | 0.0679 |
| $n$-$C_{29}$ | 0.0732 | 0.0461 | - | 0.0980 | 0.0589 | 0.0972 | 0.0461 |
| $n$-$C_{30}$ | 0.0529 | 0.0461 | 0.0469 | 0.0676 | 0.0368 | 0.0958 | 0.0332 |
| $n$-$C_{31}$ | 0.0334 | 0.0176 | 0.0260 | 0.051 | 0.0166 | 0.0482 | 0.0157 |
| $n$-$C_{32}$ | 0.0296 | 0.0257 | 0.0402 | 0.0185 | 0.0413 | 0.0438 | 0.0242 |
| $n$-$C_{33}$ | 0.032 | 0.0591 | 0.0531 | 0.0492 | 0.0578 | 0.0565 | 0.0328 |
| $n$-$C_{34}$ | 0.0529 | 0.0337 | 0.0458 | 0.0382 | 0.04 | 0.0313 | 0.0278 |
| $n$-$C_{35}$ | 0.0529 | 0.0728 | 0.0517 | 0.0667 | 0.0608 | 0.0534 | 0.0527 |
| $n$-$C_{36}$ | 0.0056 | - | 0.0059 | 0.0196 | 0.0143 | 0.0201 | - |
| $n$-$C_{37}$ | 0.0051 | - | 0.0167 | 0.0249 | - | 0.0244 | - |
| $n$-$C_{38}$ | 0.0089 | - | 0.0224 | 0.0330 | - | 0.0354 | - |
| $n$-$C_{39}$ | 0.0154 | - | - | 0.0122 | - | 0.0137 | - |
| $n$-$C_{40}$ | 0.0007 | - | - | - | - | - | - |
| Total $n$-P | 79.1248 | 84.4983 | 71.9051 | 79.3349 | 75.875 | 79.1153 | 82.1814 |
| Total $n$-P - $n$-$C_{25}$ | 2.8294 | 1.0194 | 2.3797 | 2.1817 | 1.3038 | 3.6842 | 1.6975 |
| -Odd | 77.7351 | 83.923 | 70.6494 | 78.0524 | 75.1016 | 77.1532 | 81.1763 |
| -Even | 1.3897 | 0.5753 | 1.2557 | 1.2825 | 0.7734 | 1.9621 | 1.0051 |
| Iso-P | 2.6738 | 0.8994 | 1.443 | 1.1654 | 1.1256 | 2.712 | 1.5422 |
| T-P | 81.7986 | 85.3824 | 73.3481 | 80.5003 | 77.0006 | 81.8273 | 83.7236 |
| R(excluding n-$C_{25}$) | 5.5032 | 1.9035 | 3.8227 | 3.3471 | 2.4294 | 6.3962 | 3.2397 |
| UCM | 18.2014 | 14.6176 | 26.6519 | 19.4997 | 22.9994 | 18.1727 | 16.274 |
| UCM/R | 3.3074 | 7.6793 | 6.9720 | 5.8258 | 9.4671 | 2.8411 | 5.0233 |
| CPI | | | | | | | |
| $C_{14-20}$ | 1.11 | 1.76 | 1.31 | 0.18 | 0.79 | 0.62 | 0.84 |
| $C_{20-24}$ | 1.01 | 1.23 | 1.02 | 1.06 | 0.69 | 1.86 | 1.23 |
| $C_{26-35}$ | 1.75 | 0.96 | 0.83 | 0.94 | 1.29 | 0.80 | 0.61 |
| = $C_{17}/T_n$ | 0.0470 | 0.1559 | 0.1396 | 0.3034 | 0.1009 | 0.2440 | 0.2521 |
| > $C_{17}/T_n$ | 0.9530 | 0.8441 | 0.8604 | 0.6966 | 0.8991 | 0.7560 | 0.7479 |

Fig. 1: Gas chromatograms of n-paraffins and iso-paraffins of oils extracted from water samples

This general configuration indicates petroleum hydrocarbons [5], while the predominant n- $C_{25}$ peak indicates biogenic contamination from living organisms [6]. Accordingly the real values of the petroleum hydrocarbons released in water as oil pollutants are much lower than the amounts extracted. Except for sample No. 4 (89 ppm) the values range between 4.8 - 41.4 ppm.

The amounts of the unresolved complex components (mainly Naphthenes and Aromatics) are shown to be much higher than the resolved components of petroleum origin (n- and iso- paraffins).This indicate severe weathering of spilled oil since the later components are much more naturally degradable as compared with the unresolved ones [7]. For example UCM for sample No. 1 = 18.2 %, while the others are only 5.5 %.

Table 2: High Performance Liquid Chromatographic Analysis of the Extracted Oils from Water Samples

| Concentration, µg/L | Water Sample No. | | | | | |
|---|---|---|---|---|---|---|
| | 1 | $1_{10m}$ | 2 | 3 | $3_{10m}$ | 4 |
| Benzo(g,h,l)perylene | 1315.8 | 1111.3 | 880.16 | 3216.7 | 546.844 | 1390.6 |
| Indeno(1,2,3-cd)pyrene | 0.15 | N.D. | N.D. | 5.0 | N.D. | 0.0531 |
| Total | 1315.95 | 1111.3 | 880.16 | 3221.7 | 546.844 | 1390.7 |

It is clear that n-paraffins start at n-$C_{13}$ in samples Nos. 2, $2_{10m}$, $3_{10m}$ and 4, at n-$C_{14}$ in samples Nos. 1, $1_{10m}$ and 3. However they disappear at n-$C_{35}$ in samples Nos. $1_{10m}$ and 4, n-$C_{36}$ in samples No. 3, n-$C_{38}$ in sample No. 2, n-$C_{39}$ in samples Nos. $3_{10m}$, $2_{10m}$ and at n-$C_{40}$ in sample No.1.

Total n-paraffin represents about 71.9% to 84.5% of total extracted oil content, excluding n-$C_{25}$ (of biogenic origin) it only represents about 1.0% to 3.7% of petrogenic oil content. Iso-paraffins are in the range of about 0.9% to 2.7% of oil content. Resolved compounds (R) excluding n-$C_{25}$ are in the range of 1.9% to 6.4% of oil content. Unresolved complex compounds are in the range of 14.6% to 23% of oil content.

The odd-numbered carbon n-paraffins are in the range of 70.6% to 83.9% where n-$C_{25}$ is the predominant n-paraffin ranging from 69.5 % to 83.5%. The even-carbon numbered ones have values of 0.57% to 1.96% of oil content.

**Carbon Preference Index (CPI):** This index can be expressed numerically as the ratio obtained by dividing the summation of peak areas for the odd carbon numbers by those of the even ones [8].

- n-$C_{14}$ - n-$C_{20}$, n-$C_{20}$ – n $C_{24}$ and n- $C_{26}$ - n $C_{35}$ range exhibit relatively low CPI values ranging from 0.18 to 1.76, 0.69 to 1.86 and 0.61 – 1.75, respectively, indicating mainly petroleum hydrocarbons [9].
- Unresolved / Resolved components of petroleum origin illustrate high values 2.841- 9.467 which mean the presence of weathered oils from old oil inputs [10, 11].
- ≤ n $C_{17}$/$T_n$ alkanes: They exhibit low values ranging between 0.0470 – 0.3039 indicating severe weathering processes through evaporation, dissolution, photo-oxidation and biodegradation which have greatly affected these oils in this environment [12] by the loss of the low molecular weight alkanes.
- > n $C_{17}$/$T_n$ alkanes: The n-alkanes > n $C_{17}$ are relatively more resistant to weathering processes than the lower n-alkanes < n $C_{17}$. As expected, this ratio shows higher values ranging between 0.6966 - 0.9530.

**Determination of Polyaromatics by High Performanc Liquid Chromatography:** High performance liquid chromatography (HPLC) is a very useful technique of analysis of polynuclear aromatic hydrocarbons (PAHs), which has been identified as the most suitable class of compounds for oil fingerprinting [13, 14]. The extracted oils from the studied water samples have been analyzed by HPLC and the results obtained from the analysis are given in Table 2 and HPLC chromatograms of the aromatics are given in Fig.2.

The concentrations of total polyaromatics are in the range of about 880 to 3222 µg / l for near shore surface water having the following trend 3 > 4 > 1 > 2; and from 547 to 1111 µg/l for water samples 10 m apart from shore having the trend $1_{10m}$ > $3_{10m}$. The relatively higher concentrations in the near shore samples may be due to the tourstic ships landing there.

The identified polyaromatics for near shore surface water consists of Benzo(g, h, l) perylene and Indino(1, 2, 3)pyrene. Benzo(g, h, l) perylene which has the highest concentration being in the range of about 880 to 3217 µg/l, while Indino(1, 2, 3-cd)pyrene varies from 0.053 to 4.96 µg/l. The identified polyaromatics for water samples 10 m apart from shore consists only of Benzo (g, h, l) perylene.

**Determination of Functional Groups in the Extracted Oils by Infrared Spectrometry:** This technique was used by Litherathy *et al*. [15] for the characterization of petroleum and its degradation compounds dispersed in water.

Functional groups in the extracted oils from water samples have been determined by measurement of their infrared absorption spectra in the range of wave numbers 4000 to 400 / cm. The measured infrared spectra, in wave number – % transmittance are shown in Fig. 3. The presence of the different petroleum oil hydrocarbons are confirmed by the presence of the vibrations of their functional groups as shown in the following:
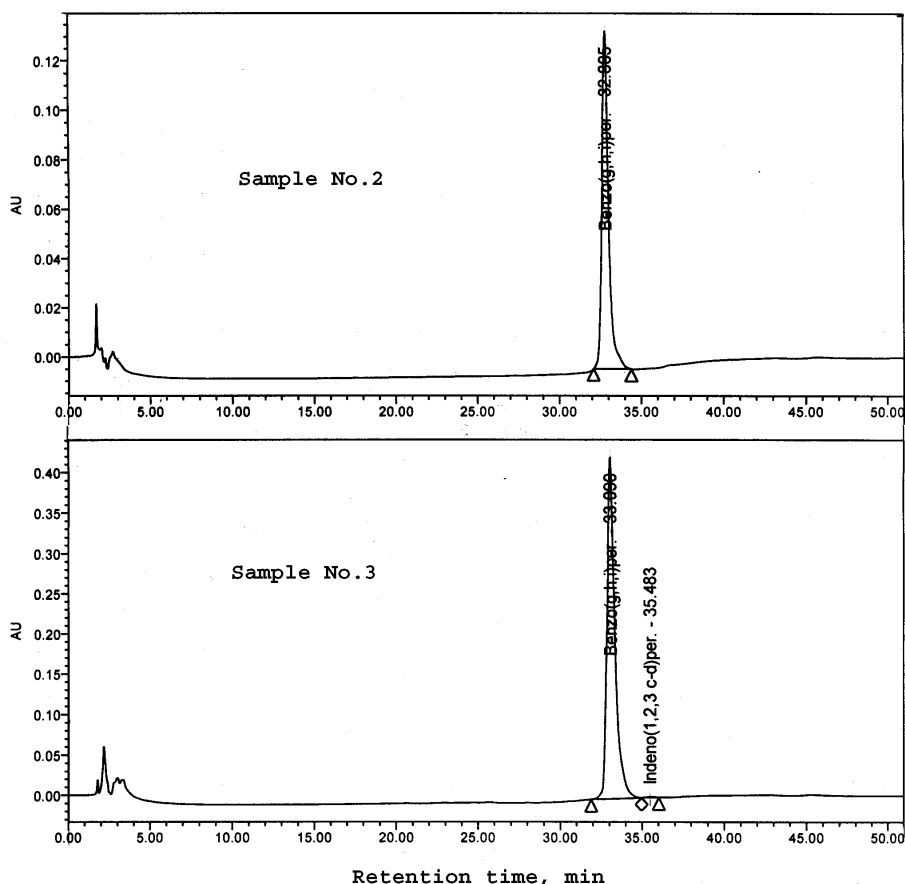
Fig. 2: High performance liquid chromatography of polyaromatics of oils extracted from water samples

**The Paraffins Hydrocarbons:**

- $CH_3$ asymmetric stretching at 2957-2958/cm
- $CH_2$ asymmetric stretching at 2925-2932/cm
- $CH_2$ symmetric stretching at 2858-2854 cm
- $CH_3$ and $CH_2$ asymmetric deformation at 1463-1459/cm
- $CH_3$ symmetric deformation at 1381-1379/cm
- Ring systems (mainly cyclohexanes) 1040-1037 and 979-955/cm
- $CH_2$ wagging at ~1350 / cm and rocking at ~ 720 / cm in long chain hydrocarbons are not detected proving the previously mentioned findings that the pollution present comes from spillages that had been subjected to weathering specially biodegradation which affect long chains much more easily.

**The Aromatic Hydrocarbons:**

- CH stretching in aromatic rings near 3030 / cm is not detected as being overlapped by other strong bands on the same region,

- C=C skeletal in-plane vibrations near 1450 / cm and near 1580 / cm (conjugated rings) are detected.
- CH out-of-plane deformation of two, three, four and five adjacent free hydrogen atoms at 860–800/cm, 810-750/cm, 770-735/cm and 710-690/cm, respectively are shown.

**The Carboxylic Acids:**

- O–C=O at 1610-1550/cm and 1420-1300/cm are present.

**Nitrogen and Sulphur Compounds:**

- C–N stretching and S=O stretching are detected at 1037 – 1040 / cm.

In conclusion the infrared spectra confirm the origin of the pollutants present as being of petroleum origin subjected to weathering effects.
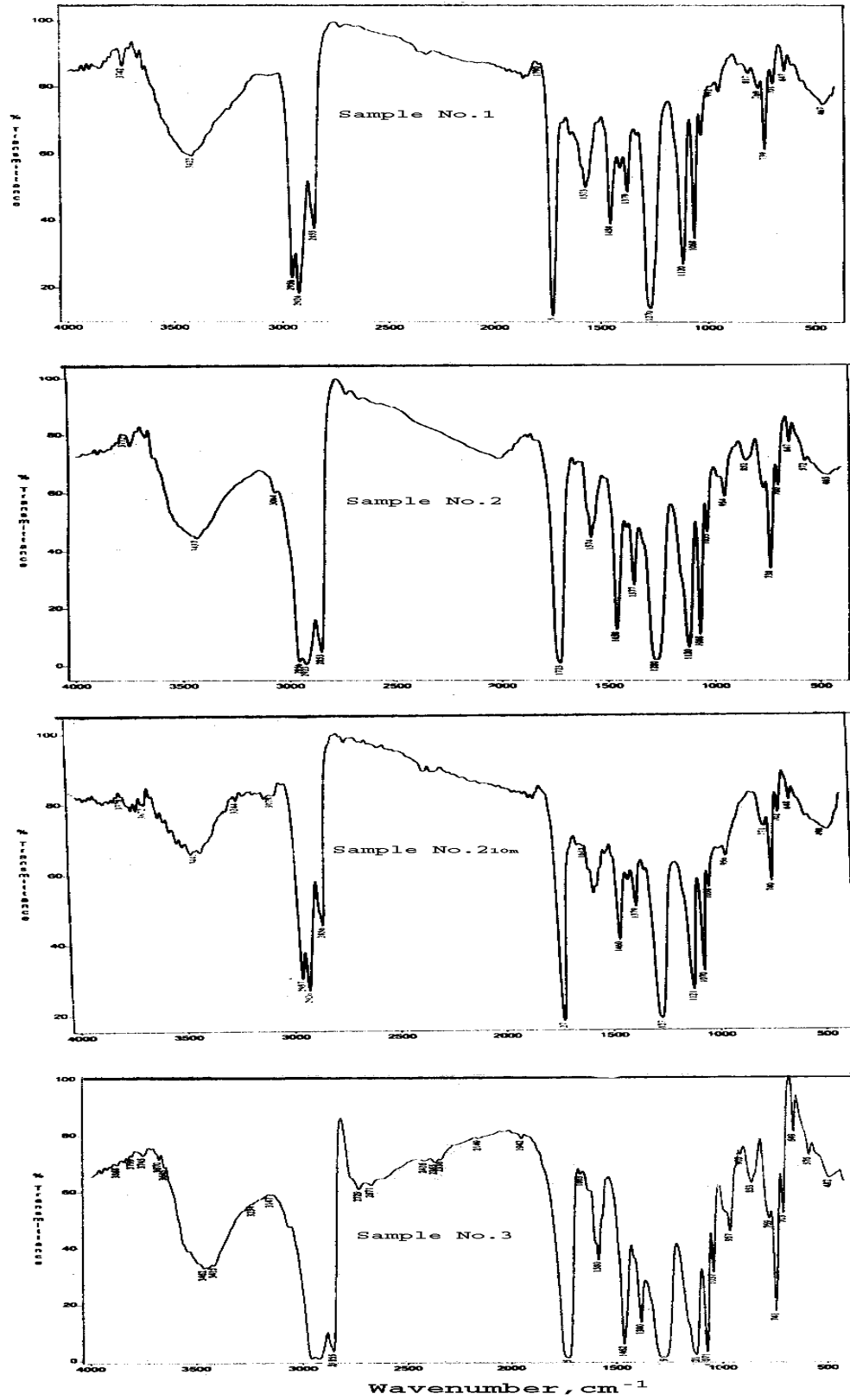
Fig. 3: Infrared spectra (wave number - % transmittance) of the oils extracted from water samples

Table 3: Gas Chromatographic Analysis of the Extracted Oils from Sediment Samples

| Concentration | Sediment Sample No. | | |
|---|---|---|---|
| | Manyal 1 | Zamalek 2 | Esna 3 |
| Oil content, mg/Kg | 547.9 | 403.5 | 1543.1 |
| $n\text{-}C_{14}$ | 1.5917 | - | - |
| $n\text{-}C_{15}$ | 1.6648 | - | - |
| $n\text{-}C_{16}$ | 0.9981 | - | - |
| $n\text{-}C_{17}$ | 1.7241 | - | - |
| $n\text{-}C_{18}$ | 1.8677 | 0.7257 | 2.605 |
| $n\text{-}C_{19}$ | 1.6389 | 0.4349 | 0.9283 |
| $n\text{-}C_{20}$ | 1.4674 | 0.1472 | 0.3142 |
| $n\text{-}C_{21}$ | 1.2783 | 0.0604 | 0.1284 |
| $n\text{-}C_{22}$ | 1.1079 | 0.0498 | 0.0993 |
| $n\text{-}C_{23}$ | 0.9783 | 0.0519 | 0.067 |
| $n\text{-}C_{24}$ | 0.7981 | - | 0.0902 |
| $n\text{-}C_{25}$ | 0.6014 | 0.2378 | 0.094 |
| $n\text{-}C_{26}$ | 0.4571 | 0.0651 | 0.0854 |
| $n\text{-}C_{27}$ | 0.3173 | 0.0917 | - |
| $n\text{-}C_{28}$ | 0.2412 | 0.1109 | 0.081 |
| $n\text{-}C_{29}$ | 0.1918 | 0.1659 | 0.183 |
| $n\text{-}C_{30}$ | 0.1638 | 0.1469 | 0.1292 |
| $n\text{-}C_{31}$ | 0.1667 | 0.1265 | 0.1038 |
| $n\text{-}C_{32}$ | 0.1072 | 0.0952 | 0.0849 |
| $n\text{-}C_{33}$ | 0.1332 | 0.1004 | 0.1314 |
| $n\text{-}C_{34}$ | 0.1362 | 0.0999 | 0.0838 |
| $n\text{-}C_{35}$ | 0.0978 | 0.0908 | 0.0715 |
| $n\text{-}C_{36}$ | 0.0481 | 0.0901 | - |
| $n\text{-}C_{37}$ | 0.0265 | 0.135 | 0.0326 |
| Total $n$-P | 17.7436 | 3.0261 | 5.313 |
| -Odd | 8.7591 | 1.4953 | 1.74 |
| -Even | 8.9845 | 1.5308 | 3.573 |
| Odd/ Even | 0.9749 | 0.9768 | 0.4870 |
| Iso-P | 2.9363 | 0.7344 | 0.2712 |
| T-P | 20.6799 | 3.7605 | 5.5842 |
| UCM | 79.3201 | 96.2395 | 94.4158 |
| UCM/R | 3.8356 | 25.5922 | 16.9077 |
| CPI | | | |
| $C_{14-20}$ | 1.1279 | 0.5993 | 0.3564 |
| $C_{20-24}$ | 0.8294 | 1.7772 | 0.5745 |
| $C_{26-35}$ | 0.8203 | 1.1106 | 1.0547 |
| $= C_{17}/T_n$ | 0.3369 | 0 | 0 |
| $> C_{17}/T_n$ | 0.6631 | 1 | 1 |

**Sediment Samples:** Oil from the studied sediment samples was extracted and the obtained results are given in Table 3, which indicate that the concentration varies from 403.5 ppm to 1543.1 ppm having the following trend 2<1<3.

**Determination of *n*-, iso- Paraffins by Gas Chromatography:** The extracted oils from the studied sediment samples were analyzed by gas chromatography to determine n-, iso- paraffins and unresolved complex hydrocarbons mainly naphenic and aromatic and the chromatograms obtained are given in Fig. 4.

It is clear that n-paraffins detected appear at $n\text{-}C_{14}$ in sample No. 1, at $n\text{-}C_{18}$ in samples Nos. 2 and 3. However they disappear at $n\text{-}C_{37}$.

Total n-paraffins represent about 3.0261 % to 17.7436% of oil content. Iso-paraffins are in the range of about 0.2712 % to 2.9363 %. Unresolved complex compounds are in the range of 79.3201 % to 96.2395 % of oil content indicating severe weathering (old spillage).

The odd-numbered carbon n-paraffins are in the range of 1.4953 % to 8.7591 %. The even-carbon numbered ones have values of 1.5308 % to 8.9845 % of oil content indicating mainly petroleum origin.

**Carbon Preference Index (CPI):**

- $n\text{-}C_{14}$ - $n\text{-}C_{20}$, $n\text{-}C_{20}$ – $n\,C_{24}$, $n\text{-}C_{26}$ – $n\text{-}C_{35}$ range exhibit relatively low CPI values ranging from 0.36 to 1.13, 0.57 to 1.78 and from 0.82 to 1.11, respectively, which indicate mainly petroleum origin.
- Unresolved/ Resolved components illustrate high values ranging between 3.8356 to 25.5922 due to the high concentrations of aromatic and naphthenic compounds which mean high weathering effect (old contamination).
- $\leq n\ C_{17}/T_n$ alkanes: They exhibit values ranging between 0 to 0.3369 indicating severe weathering processes through evaporation, dissolution, photo-oxidation and biodegradation.
- $> n\ C_{17}/T_n$ alkanes: The n-alkanes $> n\ C_{17}$ are relatively more resistant to weathering processes than the lower n-alkanes $< n\ C_{17}$. As expected, this ratio shows relatively higher values ranging between 0.66 to 1.0 due to loss of low molecular weight alkanes.

**Determination of Polyaromatics by High Performanc Liquid Chromatography:** The extracted oil from the studied Manyal sediment as representative sample has been analyzed by the high performance liquid chromatography (HPLC) Table No.4 and Fig. 5. It is clear that total polyaromatics are very minute amounts of about 1.18 µg /kg indicating relatively low molecular weight pollutants.
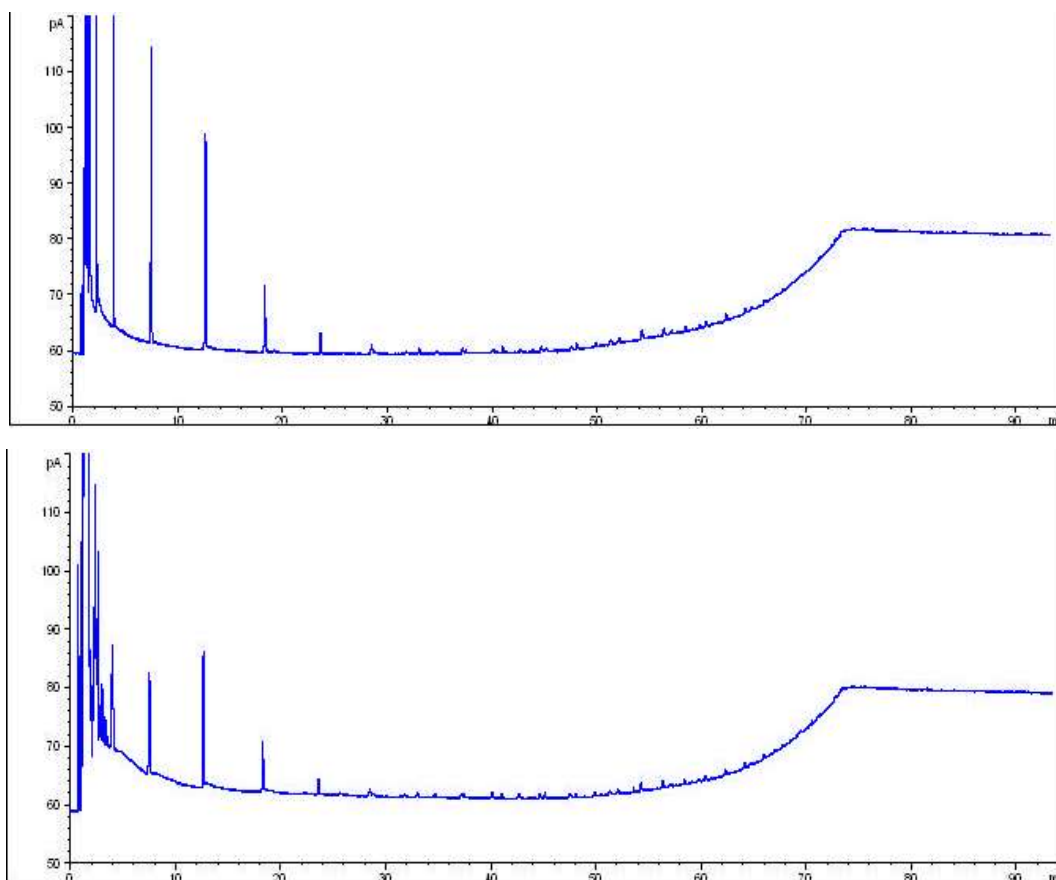
Fig. 4: Gas chromatograms of n-paraffins and iso-paraffins of oils extracted from sediment samples Nos. 2 and 3 respectively

Table 4: High Performance Liquid Chromatographic Analysis of Extracted Oils of Manyal sediment sample

| Concentration, μg/Kg | Sediment M |
|---|---|
| Naphthalene | 0.1573 |
| Acenaphthylene | 0.1706 |
| Acenaphthene | N.D. |
| Fluorene | 0.00015 |
| Phenanthrene | N.D. |
| Anthracene | 0.00563 |
| Fluoranthene | 0.00661 |
| Pyrene | 0.00277 |
| Benzo(a)anthracene | N.D. |
| Chrysene | N.D. |
| Benzo(b)fluoranthene | 0.02149 |
| Benzo(k)fluoranthene | 0.00003 |
| Benzo(a) pyrene | N.D. |
| Dibenzo(a,h)anthracene | N.D. |
| Benzo(g,h,l)perylene | 0.81654 |
| Indeno(1,2,3-cd)pyrene | N.D. |
| Total | 1.18112 |

N.D.= Not detected

**Determination of Functional Groups in the Extracted Oils by Infrared Spectrometry:** Functional groups in the extracted oils from sediment samples have been determined by measurement of their infrared absorption spectra in the range of wave numbers 4000 to 400 / cm. The measured infrared spectra, in wave number – % transmittance are shown in Fig. 6.

The presence of the different petroleum oil hydrocarbons and the oxidation products obtained during weathering are confirmed by the presence of the vibrations of their functional groups as shown in the following:

**The Paraffin Hydrocarbons:**

- $CH_3$ asymmetric stretching near 2962 and 2872 / cm, $CH_2$ asymmetric stretching near 2926 and 2853 / cm and $CH_2$ symmetric stretching near 2848 / cm are not detected as being overlapped by other very strong bands of oxidation products obtained through severe weathering.
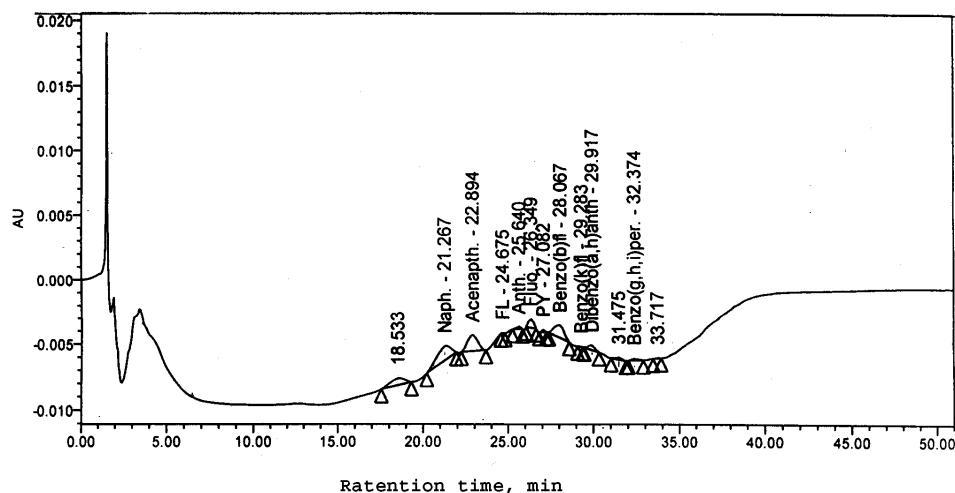
Fig. 5: High performance liquid chromatography of polyaromatics of extracted from sediment sample No. 1
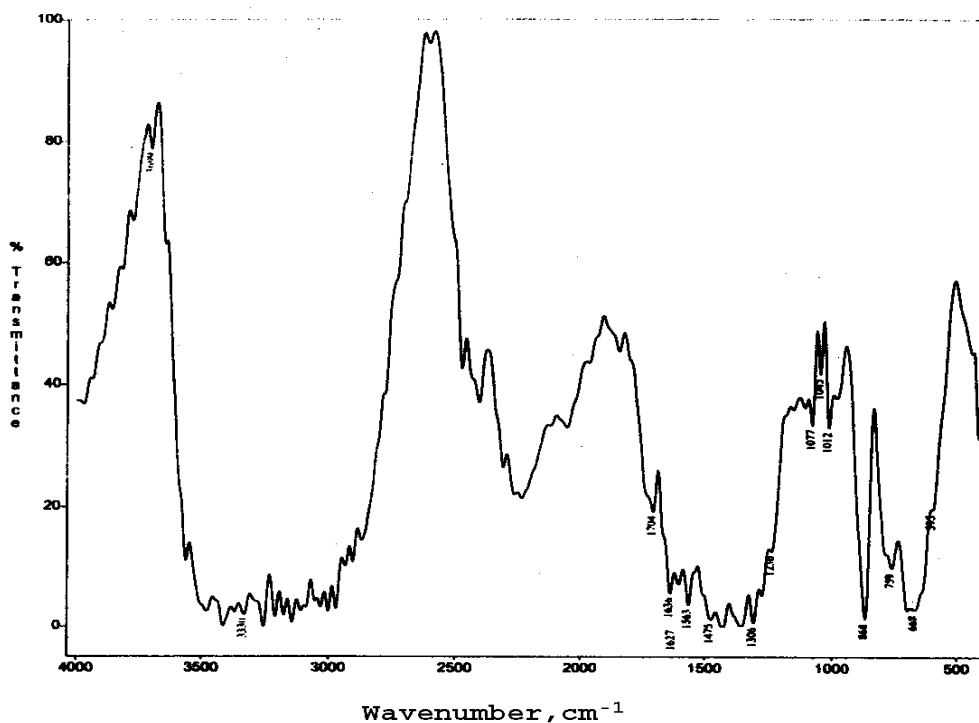


Fig. 6: Infrared spectra (wave number - % transmittance) of the oils extracted from sediment sample No. 3.

- $CH_3$ and $CH_2$ asymmetric deformation are detected at 1442 / cm and 1479 / cm, respectively.
- $CH_2$ wagging at ~1350 / cm and rocking at ~720/cm in long chain hydrocarbons are not detected proving that the previously mentioned findings that the pollution present comes from spillages that had been subjected to weathering specially biodegradation which affect long chains much more easily.
- Ring systems (mainly cyclohexanes) at 1030 / cm and 991 / cm are present.

**The Aromatic Hydrocarbons:**

- CH stretching in aromatic rings near 3030 / cm is not detected as being overlapped by other strong bands of oxidation products resulting from severe weathering proved previously.
- C=C in-plane vibrations near 1450 / cm is detected.
- CH out-of-plane deformation of two, three, four and five adjacent free hydrogen atoms at 860 – 800 / cm, 810-750/cm, 770-735/cm and 710-690/cm, respectively are fairly detected.

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**Oxidation Products:**

- O–C=O very strongly detected at 1575/cm and 1355/cm
- Free OH stretching at 3560 – 3500 / cm and bonded OH stretching at 2700 – 2500 / cm of carboxylic acids together with the free alcoholic OH at 3650 – 3590 / cm are all overlapping each other to form a very broad signal that overlaps also some other near signals.
- C=O vibrations of saturated aliphatic acids appears at 1712 / cm and Aryl acids appears at 1683 $cm^{-1}$.
  C–O stretching vibrations or OH deformation vibrations appears at 1316 $cm^{-1}$.

In conclusion comparing the infra red spectra of the oil extracted from the sediment sample with that extracted from the water samples it is clear that the oil extracted from the sediment is much more affected by weathering conditions proving that it can be originated from very old oil spill.

Generally it seems possible that the environmental hydrocarbons pollution in the river Nile comes from middle petroleum distillate fractions used in shipping activities.

**CONCLUSIONS**

- Oil pollution of surface water in river Nile seems to be mixed petrogenic (the presence of UCM hump) with biogenic hydrocarbon (n-$C_{25}$ appears as a highly predominant peak).
- The petrogenic hydrocarbon pollution in water samples seems to be old and comes from middle petroleum distillate fractions used in shipping activities. Also their relatively higher concentrations in the near shore may be due to the tourstic ships landing there.
- Biogenic contamination indicated from the predominant of n-$C_{25}$ peak was due to living organisms and biosynthesis contributed in this aquatic environment.
- Being subjected to severe environmental weathering effects, oil pollution in the river seems to be old and occidentals and the water is expected to be naturally purified mainly through photo and biodegradation.
- Oils in the sediment samples prove old contamination

**Recommendations:** Due to the increase in the number and variety of uses for water and the possible changes in the water quality due to the different human activities, it becomes of a paramount importance to keep under observation the river Nile environment, to record. Within different time intervals, the type of the water, the impacts of such activities, to identify changes or impacts due to natural causes, to gather review and digest all available information and materials concerning river Nile environment in order to take all possible regulation to

- Reserve the river in its natural state.
- Preserve the potability of the water
- Preservation and enhancement of fish and wild life.
- Preserve the safety for agricultural use, recreational use and industrial purposes

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