# N-ALKANES IN AQUATIC PLANTS OF THE HOR AL-HAMMAR MARSH OF IRAQ

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### **ABSTRACT**

Normal paraffin hydrocarbons are one of the major groups of compounds in crude oil and petroleum products. Since these compounds can be readily separated from aquatic organism using solvent extraction and liquid-solid chromatography and identified by gas-liquid chromatography, the normal paraffins can serve as indicators of petroleum pollution in the aquatic environment. It is necessary however, to differentiate between natural (or biogenic) hydrocarbons and those assimilated by the organisms from pollution scurces by comparing the natural hydrocarbons content and pattern(n-C14 to n-C37) of organisms from areas of pollution with those organism from relatively unpolluted area.

This paper presented the sources of normal paraffins from eleven aquatic plants samples from Hor al-Hammar marsh southern Iraq. These plants contained n-alkanes ranging in carbon number from C14 to C33 in addition to: isoprenoids; and a high CPI values which showed that all the components appear to be biogenic in nature.

### INTRODUCTION

After the pentration of oil into a quatic plant, the oil may travel in the intercellular spaces and possibly also in the vascular system. Cell membranes are damaged by penetration of hydrocarbon molecules, leading to leakage of cell contents and oil may enter the cells. Oils reduces transpiration rate, probably by blocking stomato and intercellular spaces. This may also be the reason for the reduction of photosynthesis processes. Other possible explanations of this, such as disruption of chloroplast membranes and inhibition caused by accumulation of end-products is valied. The effects of oils on respiration are variable among them inhibition of translocation. The severity of above effects depends on the constituents and amount of oil on the environmental conditions and on the species of plant involved (Baker,1970 and Thomas et al.,1984). The marsh region of Iraq is situated in the southern alluvial plain of the Rivers Tigris and Euphrates and has a maximum length of 210 Km a width of 170 km. Its total area of about 3500 Km² is covered by water at the time of peak flood-(AI-Saadi and AI-Mousawi,1988).

For the present study ,the largest marsh Hor Al-Hammar, was selected. Its area amounts to about 21% of the total marsh area in southern Iraq.

Little is known on the plant ecology of the marshes in Iraq (Al-Hilli, 1977 and Al-Saadi and Al-Mousawi, 1988 (1989), and no data exist on hydrocarbon contents of the aquatic plants in this area except that of Al-Saad (1994). This paper presents the result of a survey undertaken to obtain preliminary data on the present levels of n-alkanes in aquatic plants of the Hor Al-Hammar marsh.

# MATERIALS AND METHODS

Eleven different plant samples were collected from seven stations (Fig.1) to provide representative coverage of the marsh. Entire plant were collected at several points within the populations at each sampling site, thus providing samples which are representative of the populations as a whole. Plants were washed several times with marsh water at the collection site to remove as much epiphytic materials as possible, squeezed gently and placed in aluminum foil. Upon reaching the laboratory, leaves from the sampled plants were rinsed thoroughly with deionized water, dried at  $50\,^{\circ}\mathrm{C}$ ,

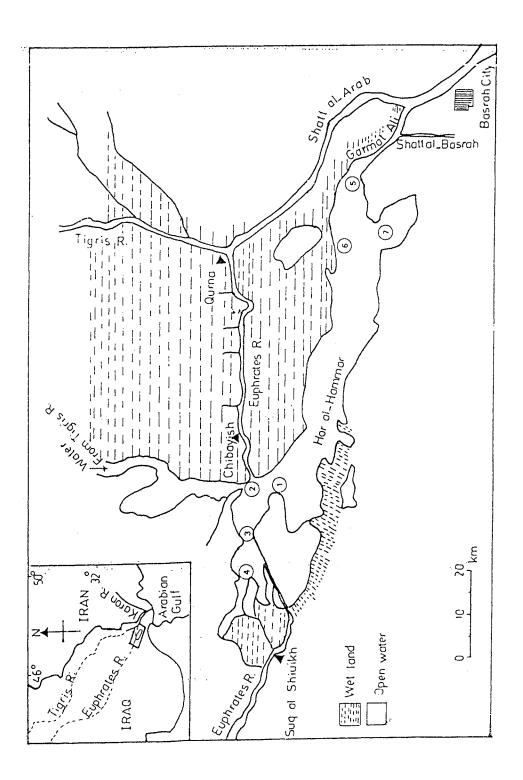


Fig.1 Sampling Locations

ground with an agate mortar, and sieved through a 1mm metal seive. Five grams of dried plant material from each sample were placed in pre-extracted cellulose thimbles and soxhlet extracted with methylenechloride. The extraction and fractionation procedures employed in the present study were based upon that of Risebrough et al., (1983).

N-alkanes were analysed by gas chromatography, employing a Perkin-Elmer Sigma 300 capillary gas chromatograph with Flame Ionization Detector (FID). A well coated open tubular fused capillary column (50m X 0.25mm i.d.) with 0.22 $\mu$ m film thickness coated with SE 30 was used. Helium was used as a carrier gas. Analyses employed the splitless injection mode, with temperature programmed from 70°C for 4 min to 300°C for 30 min. increasing at 4°C/min.

Procedural blanks consisting of all reagents and glassware used during the analysis were employed for quality control.

## RESULTS AND DISCUSSION

The concentrations of total n-alkanes in aquatic plants of the marshes of Iraq varied from  $4.57\mu g/g$  dry weight in Bacopa monniera to  $11.45\mu g/g$  dry weight in Vallisneria spiralis (Table.1).

The analysis of aquatic plant samples revealed its ability to contain hydrocarbons in their lipid pool, it could be seen that there are noticable variations in the capacity of these plants to accumulate certain hydrocarbons (Al-Saad, 1994). However consideration should be made to the fact that different species of plant have different abilities to accumulate or eliminate certain pollutants from the environment (Thomes et al., 1984). This may explain the rather high concentrations in some plant than other (Al-Saad, 1994). These concentrations were very low, with no apparent effect on the abundance of these plants.

Plant samples contained n-alkanes ranging in carbon numbers from C14 to C33 in addition to isoprenoids, phytane and pristane (Table.1 and Fig.2) with a high CPI value, indicative of biogenic origin (Simoneit,1977). All the samples exhibited n-alkanes distribution typical of plant waxes (Eglinton and Hamilton, 1963). These wax hydrocarbons were the major components in all plant samples of the area. The higher molecular weight n-alkanes exhibited a strong odd-to-even carbon number predominance (Table.1) and maximized at C25,C27 and C29 in all samples. The n-alkanes of carbon number less than C22 exhibited a distribution with essentially no predominance and a maximum at C17. The plant samples had extremely low amounts of lower molecular

Table-1-Concentration of n-alkanes in aquatic plants of the marshes of Iraq( $\mu g/g$ )dry weight

| SPECIES    | Ceratophllum<br>demersum | Potamogeton<br>lucens | Potamogeton<br>crispus | Potamogeton<br>perfoliatus | Vallisneria<br>spiralis | Najus<br>marinum | Polygonum<br>sp. | Ranunculus | Salvinia | Bacopa<br>monniera | Nymphoids<br>indica |
|------------|--------------------------|-----------------------|------------------------|----------------------------|-------------------------|------------------|------------------|------------|----------|--------------------|---------------------|
| CARBON NO. | <b>9.</b>                |                       |                        |                            |                         |                  |                  |            |          |                    |                     |
| C14        | 0.59                     | 0.18                  | 0.11                   | 0.16                       | 0.64                    | 0.54             | 0.19             | 0.21       |          | 0.33               | 0.52.               |
| C15        | 0.47                     | 0.16                  | 0.21                   | 0.17                       | 0.21                    | 0.34             | 0.18             | 0.11       | 0.11     | 0.16               | 0.55                |
| C16        | 0.17                     | 0.19                  | 0.15                   | 0.18                       | 0.42                    | 0.17             | 0.13             | 0.30       | 0.16     | 0.08               | 0.20                |
| C17        | 0.86                     | 0.98                  | 0.23                   | 0.68                       | 0.53                    | 0.32             | 0.20             | 0.46       | 0.31     | 0.12               | 0.29                |
| C18        | 0.23                     | 0.20                  | 0.20                   | 0.17                       | 0.35                    | 0.19             | 0.23             | 0.28       | 0.28     | 0.08               | 0.50                |
| C19        | 0.62                     | 0.90                  | 0.68                   | 0.73                       | 0.36                    | 0.55             | 0.42             | 0.41       | 0.88     | 0.11               | 0.30                |
| C20        | 0.15                     | 0.62                  | 0.86                   | 0.68                       | 0.28                    | 0.13             | 0.53             | 0.43       | 0.32     | 0.08               | 0.13                |
| C21        | 0.41                     | 0.89                  | 0.90                   | 0.70                       | 0.34                    | 0.74             | 0.74             | 0.68       | 0.89     | 0.10               | 0.75                |
| C22        | 0.20                     | 0.32                  | 0.43                   | 0.12                       | 0.30                    | 0.27             | 0.10             | 0.48       | 0.41     | 0.14               | 0.28                |
| C23        | 0.27                     | 0.88                  | 0.89                   | 0.82                       | 0.97                    | 0.75             | 0.69             | 0.79       | 0.93     | 0.14               | 0.89                |
| C24        | 0.38                     | 0.53                  | 0.62                   | 0.20                       | 0.65                    | 0.56             | 0.21             | 0.24       | 0.28     | 0.15               | 2.36                |
| C25        | 0.65                     | 0.86                  | 0.97                   | 0.90                       | 0.83                    | 0.11             | 0.83             | 0.81       | 0.62     | 0.28               | 0.31                |
| C26        | 0.27                     | 0.73                  | 0.50                   | 0.30                       | 0.88                    | 0.63             | 0.24             | 0.31       | 0.41     | 0.]3               | 0.43                |
| C27        | 0.16                     | 0.90                  | 0.84                   | 0.69                       | 0.89                    | 0.32             | 0.79             | 0.80       | 0.74     | 0,27               | 0.37                |
| C28        | 0.18                     | 0.63                  | 0.64                   | 0.54                       | 0.79                    | 0.24             | 0.44             | 0.56       | 0.83     | 0.18               | 0.52                |
| C29        | 0.40                     | 0.76                  | 0.78                   | 0.81                       | 0.90                    | 0.42             | 0.88             | 0.85       | 0.79     | 0.60               | 0.27                |
| .C30       |                          | 0.81                  | 0.31                   | 0.43                       | 0.70                    | 0.25             | 0.31             |            | 0.68     | 0.38               |                     |
| C31        |                          | 0.42                  | 0.42                   | 0.52                       | 0.80                    | 0.13             | 0.59             |            | 0.45     | 0.72               |                     |
| C32        |                          |                       |                        | 0.33                       | 0.23                    |                  |                  |            | 0.56     | 0.42               |                     |
| . C33      |                          |                       |                        | 0.56                       | 0.38                    |                  |                  |            |          | 0.30               |                     |
|            |                          |                       |                        |                            |                         |                  |                  |            |          |                    |                     |
| Total      | 6.01                     | 10.96                 | 9.74                   | 9.69                       | 11.45                   | 6.66             | 7.70             | 7.72       | 9.65     | 5.53               | 6.67                |
| Pristane   | 0.20                     | 0.98                  | 0.20                   |                            | 0.31                    |                  | 0.19             | 0.31       | 0.10     |                    | 0.19                |
| phytane    | 0.17                     |                       | 0.19                   |                            | 0.21                    | 0.16             | 0.20             | 0.21       | 0.]3     | 0,04               | 0.42                |
| CFI        | 1.76                     | 1.60                  | 1.54                   | 2.11                       | 1.18                    | 1.23             | 2.23             | 1.74       | 1.45     | 3,58               | 1.26                |

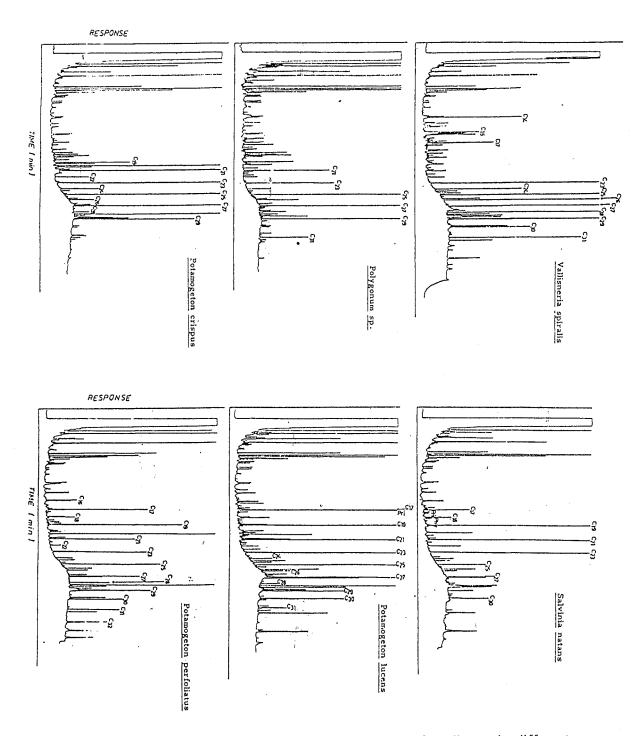


Fig.2 Gas Chromatograms (condition as cited in text ) of n-alkanes in different plant species of Hor Al-Hammar Marsh, Iraq.

weight hydrocarbons i.e. < C22 (Aceves and Grimalt, 1993).

The n-alkanes of higher plants have been throughly investigation (Eglinton and Hamilton,1963). In their waxes, the alkanes may range from C7 to C60, but rarely their significant proportions are found lying outside the range C25-C35. The major components are odd carbon numbered homologues, usually the C27, C29, C31 and C33 n-alkanes (Simoneit,1977 and GoGou et al.,1994). In constract, the interiors of higher plants contain only low concentrations of n-alkanes C16-C28 (Simoneit,1977). It is apparent, therefore, that the characteristic alkanes of these plants are found predominantly in the outer surface waxes.

N-alkanes derived from terrestrial origin are mainly associated with higher plant metabolism. The composition of all plant samples were found to contain measurable amount of n-alkanes.

The absence of UCM and high CPI values of all samples, appear to be biogenic in nature, and these compounds may be introduced into aquatic environment either fluvially or by aeoline transport (Saliot, 1981).

In conclusion, plants from Hor Al-Hammar marsh of southern Iraq were found to contain measurable amounts of hydrocarbons. The components appear to be biogenic in nature.

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# البستخلس

تعتبر الالكانات الاعتيادية واحدة من مجاميع المركبات الرئيسية المتواجدة في النفط المخام ومنتجاته، وفي الامكان فسل هذه المركبات من الكائنات المائية باستخدام تقنية الاستخلاص بالمذيبات والفسل الكروموتوغرافي، وهذه المركبات من الممكن ان تستخدم كدليل على التلوث النفطي في البيئات المائية ومن هنا يجب التبييز بين هذه المركبات المتأبية من المسادر الطبيعية (الحيرية) وتلك التي منشاها مسادر التلوث البشري، في مدا البحث تم التعرف على مسادر هذه الالكانات لاحدى عشر نوعا من البمائية المتراجدة في هور الحمار جنوب العراق، فقد بيئت الدراسة وجود المباتات المائية المتراجدة في هور الحمار جنوب العراق، فقد بيئت الدراسة وجود وقيم عالية لمعامل تفضيل الكاربون من ١٤ الى ٣٣ مع وجود مركبات البرستين والفايتين وتيم عالية لمعامل تفضيل الكاربون مما يعطي دليلا على ان مسادر هذه المركبات طبيعية (حيوية) مصدرها هذه الناتات المائية.