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# HYDROCARBONS AND CHLOROPHYLL:A CORRELATION IN THE WATERS OF THE SHATT AL-ARAB RIVER, IRAQ

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## ABSTRACT

Water samples have been collected from 5 stations along the northern sector of the Shatt Al-Arab River. Dissolved hydrocarbons ( both biogenic and anthropogenic ) have been determined in those samples spectrofluorometrically . Similarly , hydrocarbons adsorbed to suspended particles (retained on 0.45 µm GFF filter paper) have also been estimated in order to examine their removal mechanisms from Shatt Al-Arab water column via sedimentation . It was found that the distribution of dissolved and particulate hydrocarbons were ranging between 6.5 to 23.5µg/l and 1.6 to 7.5 µg/g respectively. The relatively high amount of hydrocarbons absorbed to suspended particulate matter may thus influence their mobility via the river due to the rather high sedimentation rates.

In an attempt to elucidate the role of phytoplankton as a potential source of biogenic hydrocarbons in Shatt Al-Arab River , the determination of chlorophyll a has undertaken in a representative water samples collected for this purpose simuiltaneously.Chlorophyll a values were found to vary between 0.57 to 5.25 µg/l.There was a linear correlation between particulate and dissolved hydrocarbon concentrations and chlorophyll a, measurements are (r=0.88) and (r=0.81) respectively, suggesting that these hydrocarbons may be , at least , partially originated from biogenic sources.

## INTRODUCTION

Hydrocarbon content within phytoplankton have been investigated in several studies. A significant correlation was found between the hydrocarbons content and the amount of chlorophyl present in the water (Zsolany , 1973 and 1977). Since Shatt Al-Arab River is the prime freshwater source in the area surrounding of southern Iraq , and pours about $5x10^9$ $m^3$ nutrient rich water into Arabian Gulf each year (Hartmann et al.,1971), therefore an attempt to do this type of study on the waters of Shatt Al-Arab river in Iraq has been carried out in the Marine Science Centre of the University of Basrah to see if a correlation between hydrocarbons and chlorophyll content is also present. Despite the values given according to the used procedure are purely relative ones , but the serious drawback existed with the obtained data is of great importance in the area.

Dissolved hydrocarbons(both biogenic and anthropogenic) have been determined in the samples. Similarly, hydrocarbons absorbed to suspended particles have been estimated to examine the removal mechanism from Shatt Al-Arab water column via sedimentation which is known to be of rather high rates. The measurements of hydrocarbons concentrations and chlorophyll a are suggesting that these hydrocarbons may be explained as being , at least , partially due to biological activities , so the aim of this study was find out such conclusion.

## MATERIALS AND METHODS

The geographical locations of the sampling area and positions of the sampling sites are illustrated in (Fig. 1). Sampling was concentrated along the main axis of the estuarian rather than tributaries.

Subsurface 1 m depth water samples have been collected at low tide from all stations.In order to keep contamination to minimum, the samples were taken as soon as possible after the vessel had stopped. A weighted bottle that was attached to a small buoy by mean of a 1 m long rope was used. This device could be tossed a considerable distance from the vessel and sank so rapidly that water from 1 m depth was collected. This procedure has the advantage that the depth of the sample was independent of the vessel's oscillation (Zsolnay, 1977):In all cases the chlorophyll and hydrocarbon samples were taken from the same bottle. For the hydrocarbon determinations samples of 25 liter of water were used, while for the chlorophyll a measurements 3 liters were taken. The chlorophyll samples were filtered through Millipore filters

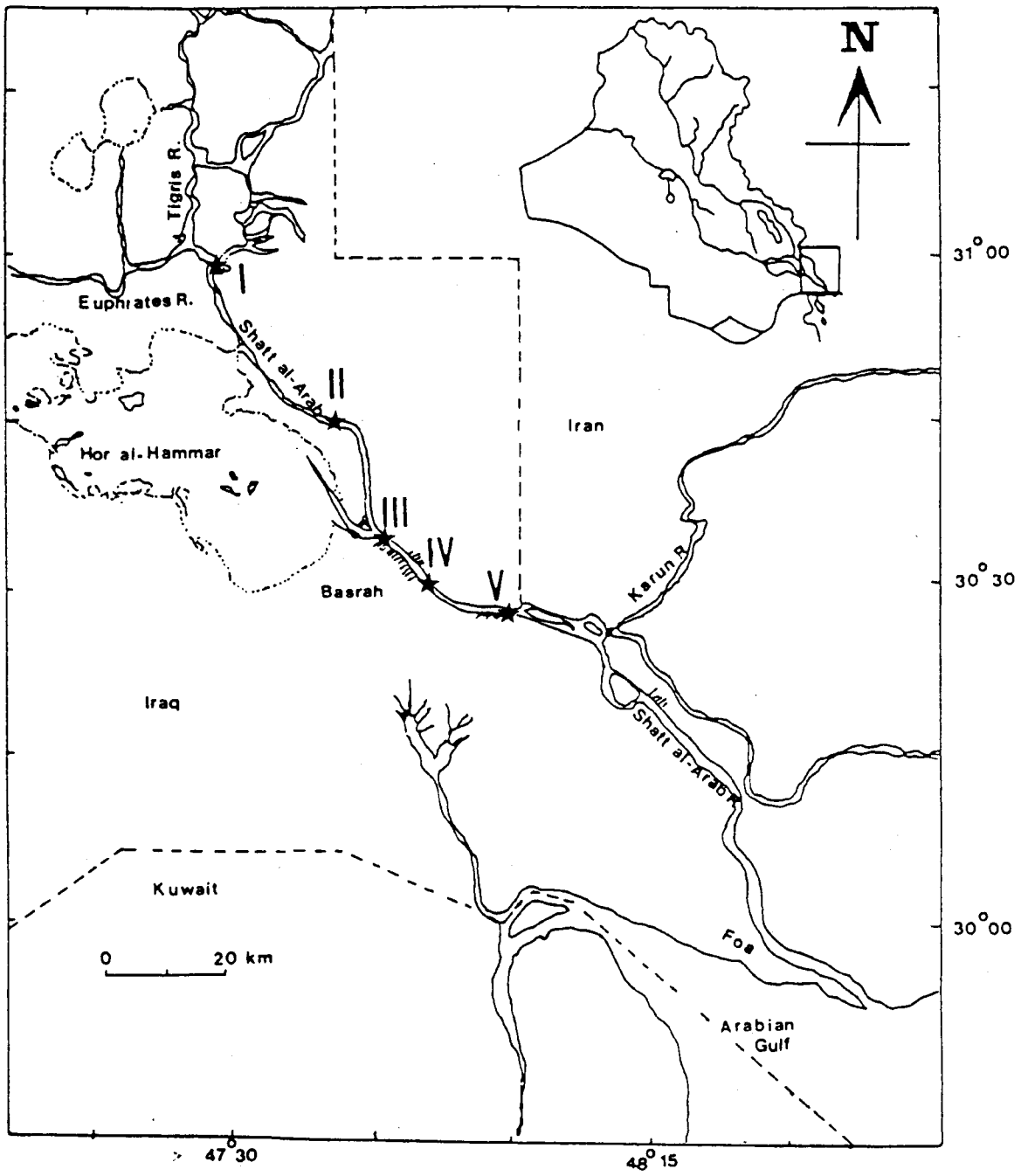


Figure (1) : Positions of sampling sites.

with a pore size of 0.45 µm. The filters were stored in the dark in a desiccator at about 20 °C.The filters were measured for chlorophyll a by the Richards and Thompson (1957) method as has been described by Strickland and Parsons (1972) using spectrophotometry by a Pye Unicam SP30 Spectrophotometer.

The method used to determine dissolved hydrocarbons in water followed the spectrophotometric method based upon that adopted for the IGOSS project(IOC/WMO,1976).Such a technique has been employed by several research works for the estimation of oil residue in water (Zitko and Garson, 1970 ; Keizer and Gordon, 1973; Law, 1981 and DouAbul and Al-Saad , 1985). For the present study an RF 540 Shimadzu Spectrofluorometer was used for measurement.

For particulate hydrocarbons determination a glass fiber filter papers (GFF) with a pore size of 0.45 µm were used. The filters were extracted by soxhlet extraction with cyclohexane, firstly, for 24 hours, then after a volume of 25 liters of water was filtered through them. The procedure used for extraction and analysis of hydrocarbons in the particulate was based upon that in (IOC/WMO, 1976 and 1982). All glassware were washed , acid bathed , and rinsed with distilled water , acetone , and n-hexane before being used . API Kuwait crude oil was chosen as an arbitrary standard.For the extracted hydrocarbons to be charecterized some samples were analysed by gas liguid chromatography. For this purpose a Perkin Elmer Sigma 300 Capillary Chromatography was used.

## RESULTS AND DISCUSSION

The hydrocarbons (dissolved and particulate) values are given in Tables (1) and (2) respectively. The chlorophyll a results are given in Table (3).

Hydrocarbons were expressed in the Kuwait crude oil equivalent concentrations.

Chlorophyll is one of the few complex organic compounds which has been (historically) routinely measured in waters as an indicator of photosynthetic activities (Yentsch and Menzel, 1963 and Harvey, 1966).

This study showed that chlorophyll a content is ranging between 0.59 µg/l at station I and 5.25 µg/l at station IV , similarly concentrations of dissolved hydrocarbons are 6.5 23.5 mg/l in these stations while those for particulate hydrocarbons are 1.6 and 7.5 mg/g respectively.

The direct relationship is very obvious between the two components,chlorophyll a and hydrocarbons due to eutrophication which increases the population of phytoplankton. The

Table (1) : Concentration of dissolved hydrocarbons observed in the Shatt Al-Arab River water.

| Site No. | Concentration in µg/l * Range | Aversge | Standard Deviation | Standard Error µg/l |
|---|---|---|---|---|
| I | 5.2- 7.6 | 6.5 | 0.927 | 0.380 |
| II | 8.8-14.6 | 11.3 | 2.030 | 0.833 |
| III | 13.5-16.6 | 14.7 | 1.166 | 0.477 |
| IV | 22.3-25.8 | 23.5 | 1.330 | 0.547 |
| V | 16.5-20.3 | 18.4 | 1.280 | 0.526 |

* Values obtained from 6 samples for each station.

Table (2) : Concentration of particulate hydrocarbons observed in the Shatt Al-Arab River water.

| Site No. | Concentration in µg/g * Range | Aversge | Standard Deviation | Standard Error µg/g |
|---|---|---|---|---|
| I | 1.4-1.8 | 1.6 | 0.141 | 0.057 |
| II | 1.3-3.2 | 2.3 | 0.748 | 0.306 |
| III | 2.0-4.5 | 3.1 | 0.880 | 0.361 |
| IV | 6.3-9.1 | 7.5 | 0.980 | 0.404 |
| V | 4.2-6.8 | 5.2 | 0.980 | 0.404 |

* Values obtained from 6 samples for each station.

Table (3) : Concentration of chlorophyll a in the water of Shatt Al-Arab River.

| Site No. | Concentration in µg/l * Range | Aversge | Standard Deviation | Standard Error µg/l |
|---|---|---|---|---|
| I | 0.55-0.63 | 0.59 | 0.030 | 0.012 |
| II | 0.63-0.77 | 0.72 | 0.050 | 0.020 |
| III | 0.90-1.11 | 0.98 | 0.072 | 0.029 |
| IV | 4.65-6.32 | 5.25 | 0.603 | 0.247 |
| V | 0.90-2.06 | 1.20 | 0.048 | 0.175 |

* Values obtained from 6 samples for each station.

very abundant phytoplankton species in Shatt Al-Arab River are Cyclotella meneghiniana , Synedra ulna and Cocconies placentula , often the standing crop of thses species is higher in winter season than in summer.

Huq et al. (1978) and Antoine (1983) showed that the seasonal distribution of chlorophyll a in Shatt Al-Arab is a bimodal with a maximum value in autumn.

DouAbul and Al-Saad (1985) stated that there is a seasonal variation of oil residue in the waters of Shatt Al-Arab with maximum values in autumn (Oct.) also.

This study may indicate that the direct correlation between chlorophyll a and hydrocarbons as had been determined here simultaneously gives, al least , an evidence for the biological origin of hydrocarbons in the waters of Shatt Al-Arab River.

The highest percentage of n-alkanes are generally as sociated with chlorophyll a concentration , providing an evidence for the biological origin for the hydrocarbons encountered particularly compounds between n-C21 and n-C36 with maximum centered around n-C24 (Goutx and Saliot, 1980). Figure ( 2 ) shows two chromatograms of dissolved and

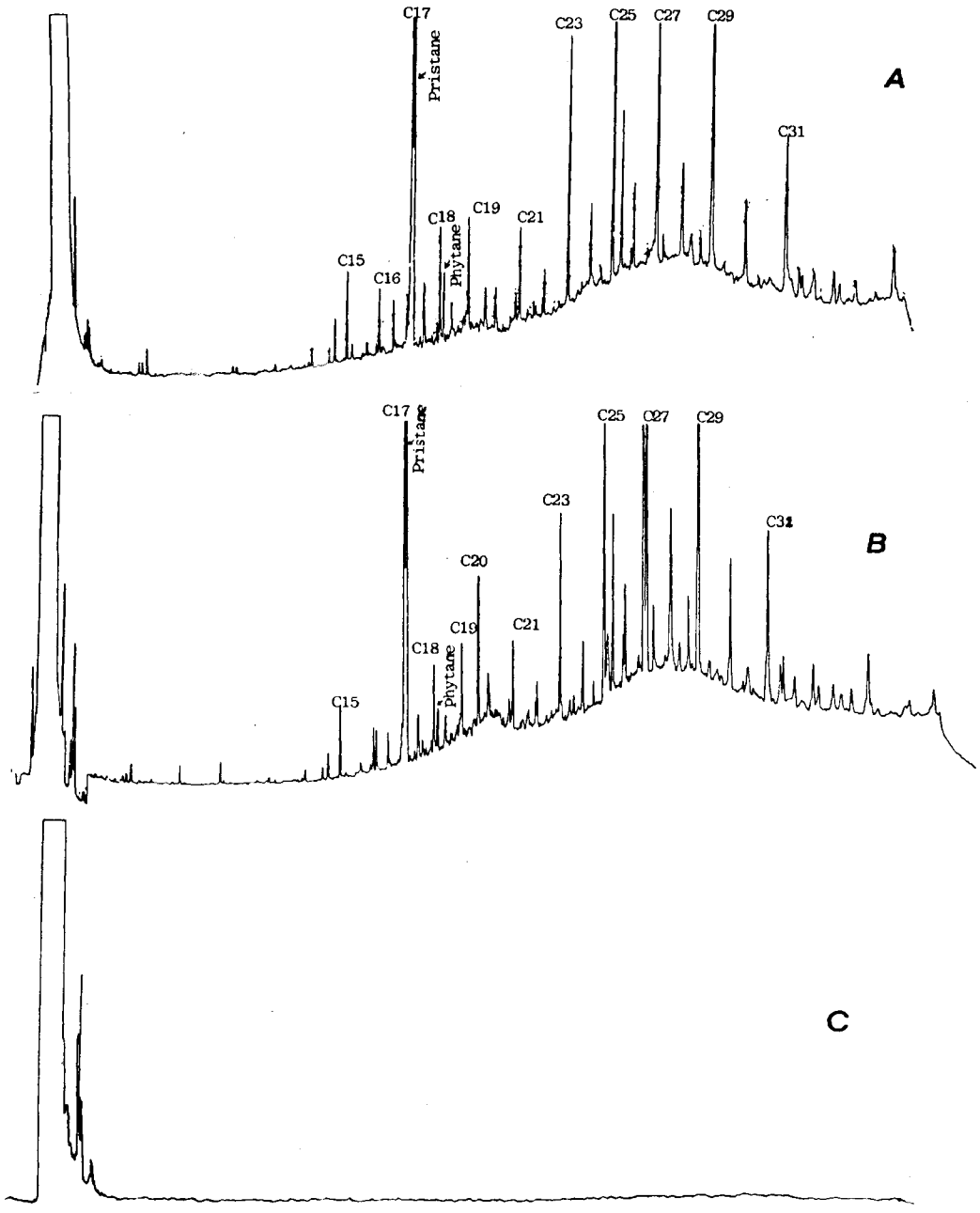


Figure (2):F.I.D Capillary gas Chromatograms of Hydrocarbons from Shatt Al-Arab River.
A: Dissolved , B: Particulate, C: Blank.
SP-2100 WCOT coloumn 50 m , He carrier gas , 1.5 Ml/Min. temperature programmed 60 - 280 °C , 4C /Min, Splitless injection. Perkin-Elmer G.C.

particulate hydrocarbons against a blank chromatogram which are chosen for the characterization of the hydrocarbon compounds (Mckay and Latham, 1972). Studying those chromatograms will illustrated the presence of those compounds such as n-C17, n-C19, n-C21, n-C25, n-C27 and n-C29 which appear to confirm the recent biogenic origin of the hydrocarbons (Marty and Saliot, 1976).

Statistically,the data were calculated according to the equation of Zsolnag (1977) :

$$H = -1.4 + 3.26\ Ch - 0.325\ Ch^2$$

Where H and Ch are the hydrocarbons and chlorophyll concentrations in mg/l,respectively. This equation explained 52% of the variance in the hydrocarbons distribution (Zsolnay,1977). Hydrocarbons in this study has a significant correlation coefficient with chlorophyll (r=0.99); while we found the correlation between chlorophyll a and dissolved hydrocarbons ( r=0.81 ) and the correlation between chlorophyll a and particulate hydrocarbons (r=0.88) in the waters of Shatt Al-Arab River which are both regarded to be significant at a probability level well below 0.001. The significant correlation is suggesting that thses hydrocarbons may be,at least,partially originated from biological activities in the waters of Shatt Al-Arab River.

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## العلاقة بين كمية الكلوروفيل ا والهايدروكاربونات في مياه شط العرب / العراق

### المستخلص

تم جمع عينات مائية من خمس محطات في الجزء العلوي (الشمالي) من نهر شط العرب لغرض تحديد المركبات الهايدروكاربونية الذائبة بطريقة اللصف ، كذلك قيست المركبات الهيدروكاربونية العالقة بالجزئيات بعد ترشيحها بورق ترشيح (GFF 0.45 $\mu m$) لغرض التعرف على

مدى مساهمة هذه الجزئيات العالقة بترسيب المركبات الهيدروكاربونية في شط العرب.

وجدت معدلات التوزيع تتراوح بين 6.5 - 23.5 مايكروغرام باللتر للهايدروكاربونات الذائبة وللعالقة 1.6 - 7.5 مايكروغرام بالغرام. وقد وجد ايضا ان كمية الهايدروكاربونات العالقة بالجزئيات العالقة تكون عالية نسبيا وهذا مما قد يوثر على حركتها وانتشارها في مياه شط العرب نتيجة لمعدلات الترسيب العالية في النهر.

وفي محاولة لتوضيح ان العوالق النباتية تلعب دورا مهما كمصدر للهايدروكاربونات في شط العرب فان عينات مائية اخرى اخذت في نفس الوقت لقياس كمية المادة الخضراء (كلوروفيل ا) وكانت نتائج القياس تتراوح بين 0.57-5.25 ملغرام باللتر.

من العلاقات الاحصائية تبين وجود علاقة خطية قوية بين كل من الهايدروكاربونات العالقة والكلوروفيل وبين الهايدروكاربونات الذائبة والكلوروفيل ايضا حيث وجدت قيمة المكافي الخطي للاولى 0.88= $r^2$ وللثانية 0.81= $r^2$ ومن هذا يمكن الاستدلال ولو بصورة جزئية على الاقل ان وجود المركبات الهايدروكاربونيةفي مياه شط العرب ياتي من مصادر حية ومن فعاليات بايولوجية.