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Distribution and seasonal variations of hydrocarbons in the molluscs of Shatt Al-Arab river

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Abstract The seasonal variations of hydrocarbons in molluscs of Shatt Al-Arab river have been studied. These species of molluscs were the snails, *Lymnaea auricularia*, *Theodoxus jordani*, *Physa acuta*, *Melanopsis nodosa* and *Melanoides tuberculata* while the bivalves were *Corbicula fluminea* and *Corbicula fluminalis*. The molluscs were collected from different locations of Shatt Al-Arab river (along the region extended from Abu Al-Khasib to Garmat-Ali) during 2004 and 2005. Each species consisted of at least 3500 adults and uniform size of individuals. The hydrocarbons were extracted and analyzed by spectroflurometer. The concentrations of total hydrocarbons referred to (Basrah regular crude oil equivalents) in different molluscs species varied from 1.93 µg/g dry weight in the *T. jordani* to 9.83 µg/g dry weight in the *C. fluminea* during Summer and from 2.90 µg/g dry weight to 22.37 µg/g dry weight during Autumn. While ranges from 3.58 µg/g dry weight to 26.56 µg/g dry weight and from 2.60 µg/g dry weight to 14.13 µg/g dry weight during winter and spring. This study confirmed higher concentrations of hydrocarbons in the mollusc's species during winter and autumn while lower concentrations were measured during summer and spring. This is due to several factors which could act to produce such seasonal variations.

Introduction

Molluscs are well known for their ability to accumulate hydrocarbons (and other pollutants) and have been employed as indicators of hydrocarbons contamination in many parts of the world, such as by the mussel watch programme (Farrington and Tripp, 1993). Shatt Al-Arab river have many species of mollusca, the common dominats members of the benthic macrofauna are the the snails, *Lymnaea auricularia*, *Theodoxus jordani*, *Physa acuta*, *Melanopsis nodosa*, *Melanoides tuberculata* and the bivalves, *Corbicula fluminea* and *Corbicula fluminalis*. UNEP (1993), Cajaraville *et al.* (1995) and NRC (2003) reported that the indigenous species of molluscs represent ideal subjects for evaluating contaminants in the aquatic environment because they are sedentary and, excepting the larval sojourn, spend their entire lives in the same location; molluscs populations inhabit water which are polluted by domestic sewage, petroleum by–products and industrial waste products; they tend to concentrate almost all noxious substances in the environment in their body; they are relatively easy to locate and sample; it is possible to obtain or locate spat (young molluscs that have recently metamorphosed from the free–swimming larval stage to the permanently attached form) and thus, it is possible to monitor the rate of uptake and incorporation of various toxic chemical in molluscs populations starting with essentially zero-aged animals; their ubiquitous distribution permits comparisons to be made with other workers; and large number of molluscs can be analyzed and examined.

The hydrocarbons in Shatt Al-Arab river water are originated from different sources. Bedair and Al-Saad (1992) reported that the hydrocarbons in Shatt Al-Arab estuary were likely originated from boating activities, runoff from land and introduction via sewage effluents. Boats with outboard motors use a mixture of gasoline and lubricating oil as fuel and most of the oil is discharged with the exhaust into the water. The storm water runoff from the urban areas was found to be the primary source of petroleum hydrocarbons in the area (Al-Mudaffer *et al.*, 1990). The storm water contained higher levels of hydrocarbons derived from lubricating oils as pyrolytic products released by automobile traffic. This may also constitute a major source of hydrocarbons found in the river, since the used motor oil from automobiles may be discharged discriminately into the environment and then reaches the river via runoff. Also DouAbul and Al-Saad (1985) indicated that oil pollution in Shatt Al–Arab river was possibly originated from diverse sources such as oil refineries, rural runoff, electricity generating stations, sewage discharges and river transportation activities. However, they considered sewage discharge and urban runoff as the most significant sources of oil entering Shatt Al-Arab river. Al-Saad (1995) also reported that many aquatic organisms of Shatt Al-Arab river including plants, algae, zooplankton, bacteria and fish were capable to synthesize biogenic hydrocarbons.

The objective of present study was to determine the distribution and seasonal variation of hydrocarbons in the species of molluscs collected from different location in Shatt Al–Arab river.

Materials and Methods

Specimens of seven species of molluscs, *L. auricularia*, *T. jordani*, *P. acuta*, *M. nodosa*, *M. tuberculata*, *C. fluminea* and *C. fluminalis* were collected from Shatt Al–Arab river (along the region extended from Abu-Al-Khasib to Garmat-Ali) during 2004 and 2005 (Figure 1). At least 3500 adult

The tissues of the animals were pooled and macerated in a food liquidizer from which at least 3 replicates of 15g each were freeze-dried, grounded and sieved through a 63µ metal sieve. The procedure of Grimalt and Oliver (1993) was used for hydrocarbons extraction from mollusc's tissues. Ten grams of dried molluscs tissues were placed in a pre-extracted cellulose thimble and soxhlet extracted with 150ml methanol: benzene (1:1 ratio) for 24-hours. The extract was then transferred into a storage flask. The sample was further extracted with a fresh solvent. The combined extracts were reduced in volume to ca 10 ml in a rotary vacuum evaporator. They were then saponified for 2- hours with a solution of 4 N KOH in 1:1 methanol: benzene. After extraction of the unsaponified matter with hexane, the extract was dried over anhydrous Na2 SO4 and concentrated by a stream of N2 for UVF analysis. A shimadzo RF-540 spectroflurometer equipped with a DR –3 data recorder was used to determine total petroleum hydrocarbons. The basis quantitative measurements were made by measuring emission intensity at 360 nm with excitation set at 310 nm and monochrometer slits of 10 nm.

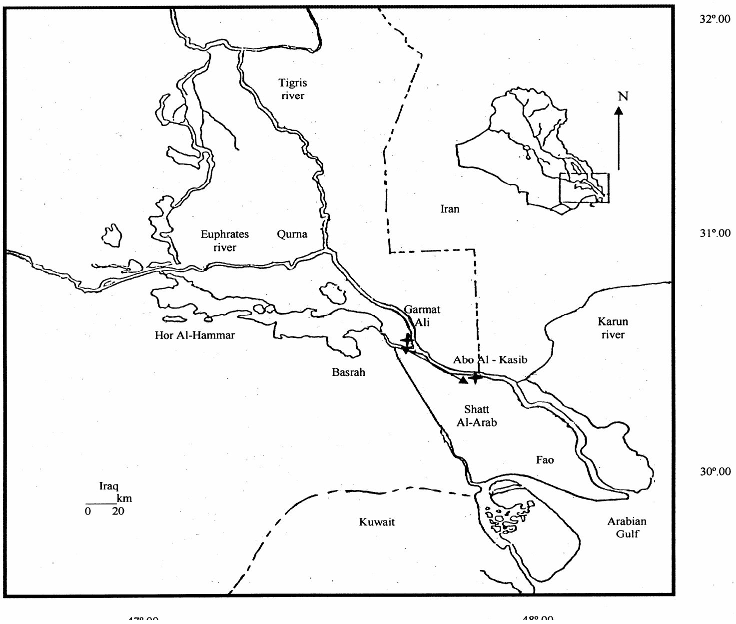

Figure 1. Map showing Shatt Al-Arab river and sampling locations.

Throughout the procedure, a great care is taken to ensure that samples are not contaminated; it is very important to avoid an unnecessary exposure of the samples (whether the solvent or the final extract) to the atmosphere or other potential contamination sources. However, procedural blanks of all reagents and glassware that were used during the analysis were periodically determined. It is preferred to eliminate contamination sources rather than adjusting or correcting the data that were actually obtained according to the blank value.

The fluorescence intensity of the sample analyzed was compared with the fluorescence of a reference solution (having almost the same concentration as the unknown extract) or to a series of reference solution (wherever, the measurement of fluorescence of the sample took more than one day).

The fluorescence of reference solution was measured at least once a day under identical instrumental conditions. The reference oil was used in the spectroflurometer obtained from Iraqi South Oil Company (Basrah regular crude oil) (Fig. 2).

Results and Discussion

The concentrations of hydrocarbons were measured seasonally in species of molluscs of Shatt Al-Arab river. The concentrations of hydrocarbons varied from 1.93 µg/g dry weight in the *T. jordani* to 9.83 µg/g dry weight in the *C. fluminea* during Summer and from 2.90 µg/g dry weight to 22.37 µg/g dry weight during Autumn, whereas they were from 3.58 µg/g dry weight to 26.56 µg/g dry weight and from 2.60 µg/g dry weight to 14.13 µg/g dry weight during winter and spring, respectively (Table 1) and (Figure 3).

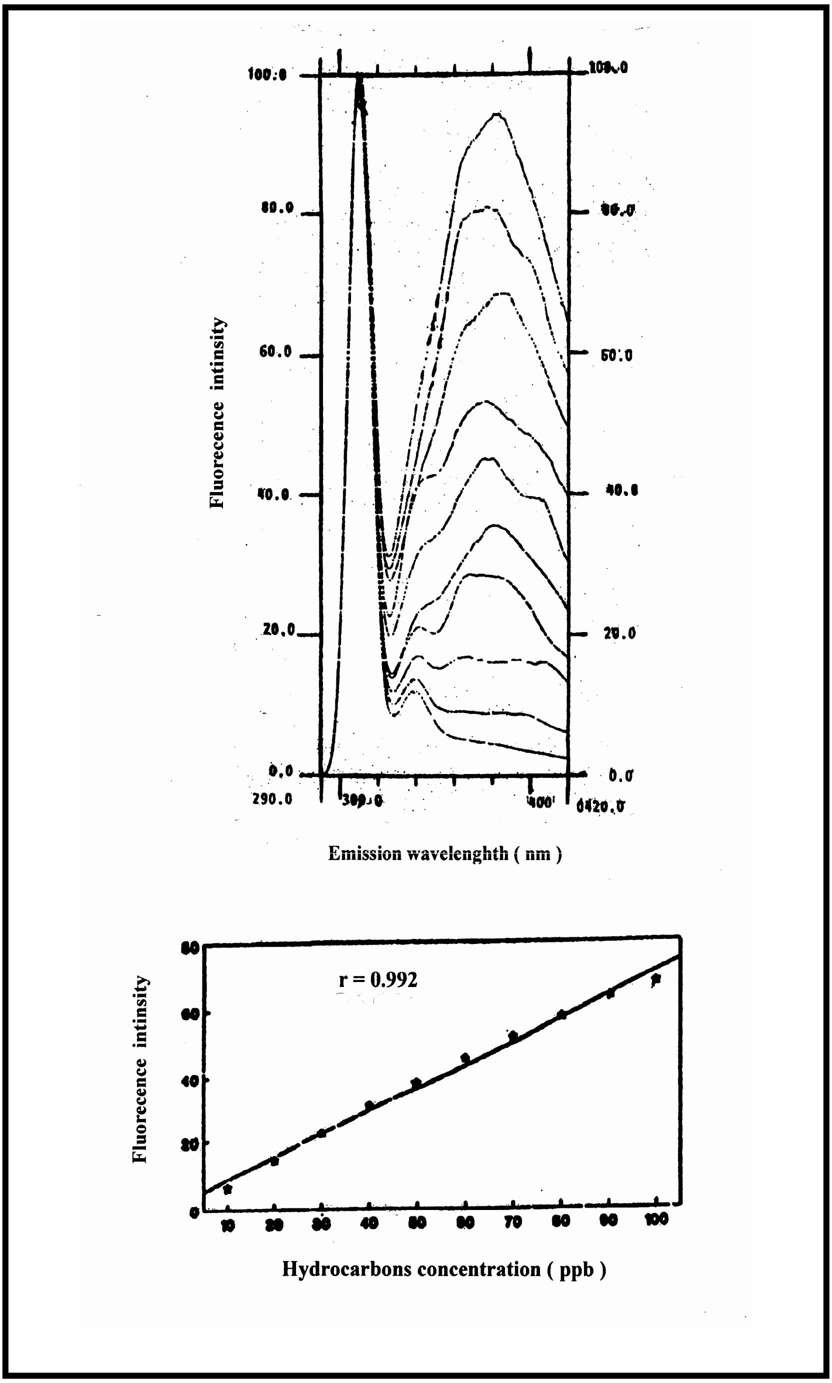

Figure 2. Fluorescence spectra with calibration curve of standard crude oil (Basrah regular).

It is clear that the higher concentrations of hydrocarbons were recorded in all species of molluscs during winter and autumn. The lowest levels were recorded during summer and Spring (Table 1) and (Figure 4). The hydrocarbons were probably biogenic or anthropogenic accumulated into species of molluscs tissues from phytoplankton or through water, either from solution or adsorbed to suspended particles, while feeding and retained as part of the lipid energy store and utilized during the winter. The same conclusion had been derived by (Cripps and Priddle, 1995).

In addition, several factors acting either alone or in combination could produce the seasonal variations in the concentrations of hydrocarbons in Shatt Al-Arab river (Al-Saad, 1995) which will accumulate later in tissues of the river organisms (including molluscs). It was found that the concentrations of hydrocarbons in Shatt Al-Arab river water varied inversely with water temperature (Al-Saad, 1995).

Al-Saad and Al-Timari (1993) and Al-Saad (1995) documented that temperature is the most important factor governing the removal of hydrocarbons in the water of Shatt Al-Arab river by evaporation. In addition to the direct effect of temperature on the evaporation of hydrocarbons from water of Shatt Al-Arab river, increase in temperature favors bacterial degradation process (Abdul-Retha, 1997).

Table 1. Concentrations of total hydrocarbons (μg/g dry weight) in the species of molluscs tissues from Shatt Al-Arab river during 2004 -2005.

Species	Concentrations of Total Petroleum Hydrocarbons			
	Summer	Autumn	Winter	Spring
L . auricularia	2.82 ± 0.04	3.53 ± 0.06	5.27 ± 0.07	3.72 ± 0.04
T . jordani	1.93 ± 0.06	2.90 ± 0.04	3.58 ± 0.08	2.60 ± 0.02
P . acuta	2.60 ± 0.08	3.06 ± 0.04	3.91 ± 0.05	3.33 ± 0.01
M . nodosa	4.28 ± 0.04	6.27 ± 0.04	8.16 ± 0.05	5.55 ± 0.03
M . tuberculata	3.21 ± 0.03	5.15 ± 0.05	6.85 ± 0.04	4.23 ± 0.06
C . fluminea	9.83 ± 0.06	22.37 ± 0.05	26.56 ± 0.02	14.13 ± 0.06
C . fluminalis	5.49 ± 0.08	7.25 ± 0.05	9.30 ± 0.05	6.54 ± 0.08

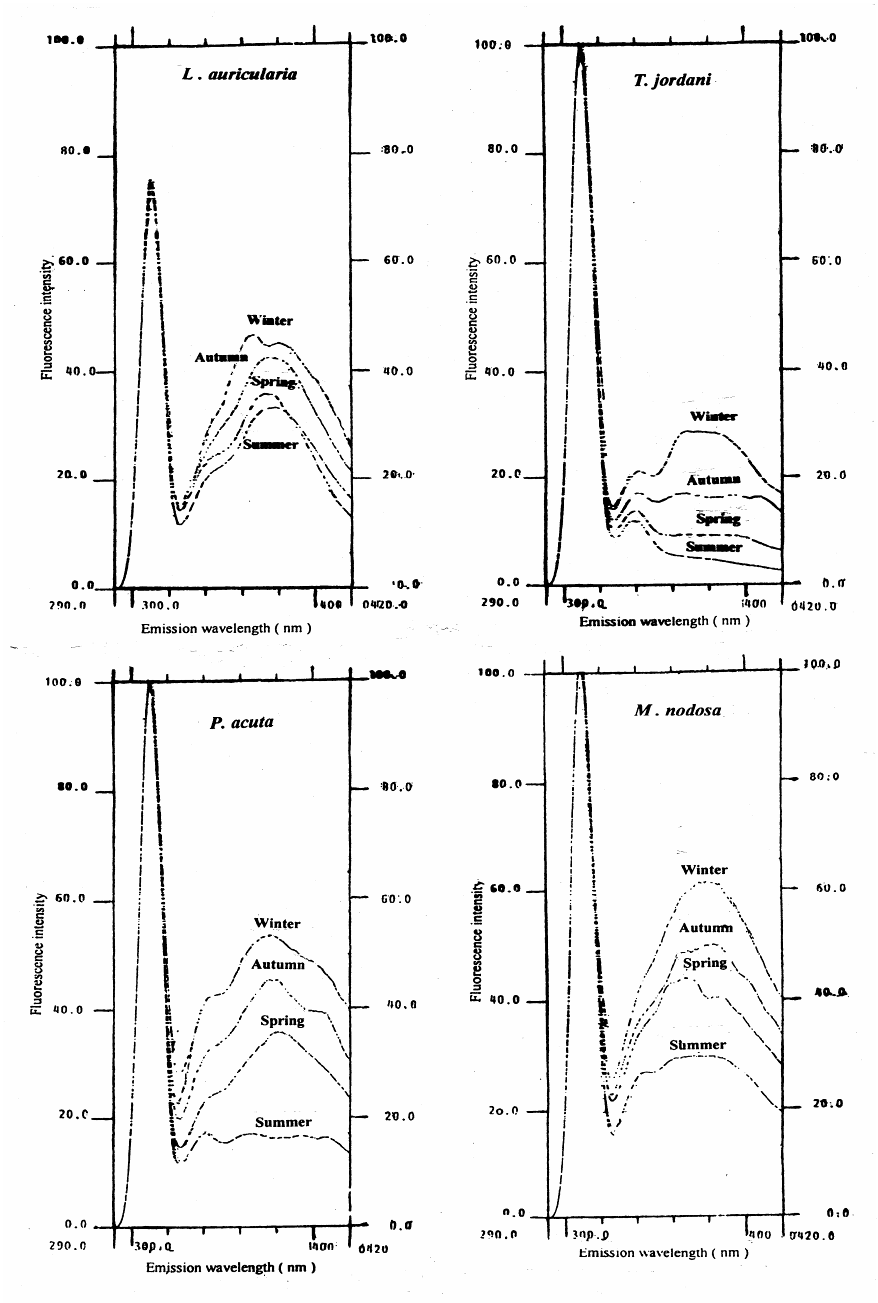

Figure 3. Fluoresence spectra of total hydrocarbons concentrations in the species of molluscs tissues from Shatt Al–Arab river during 2004 - 2005.

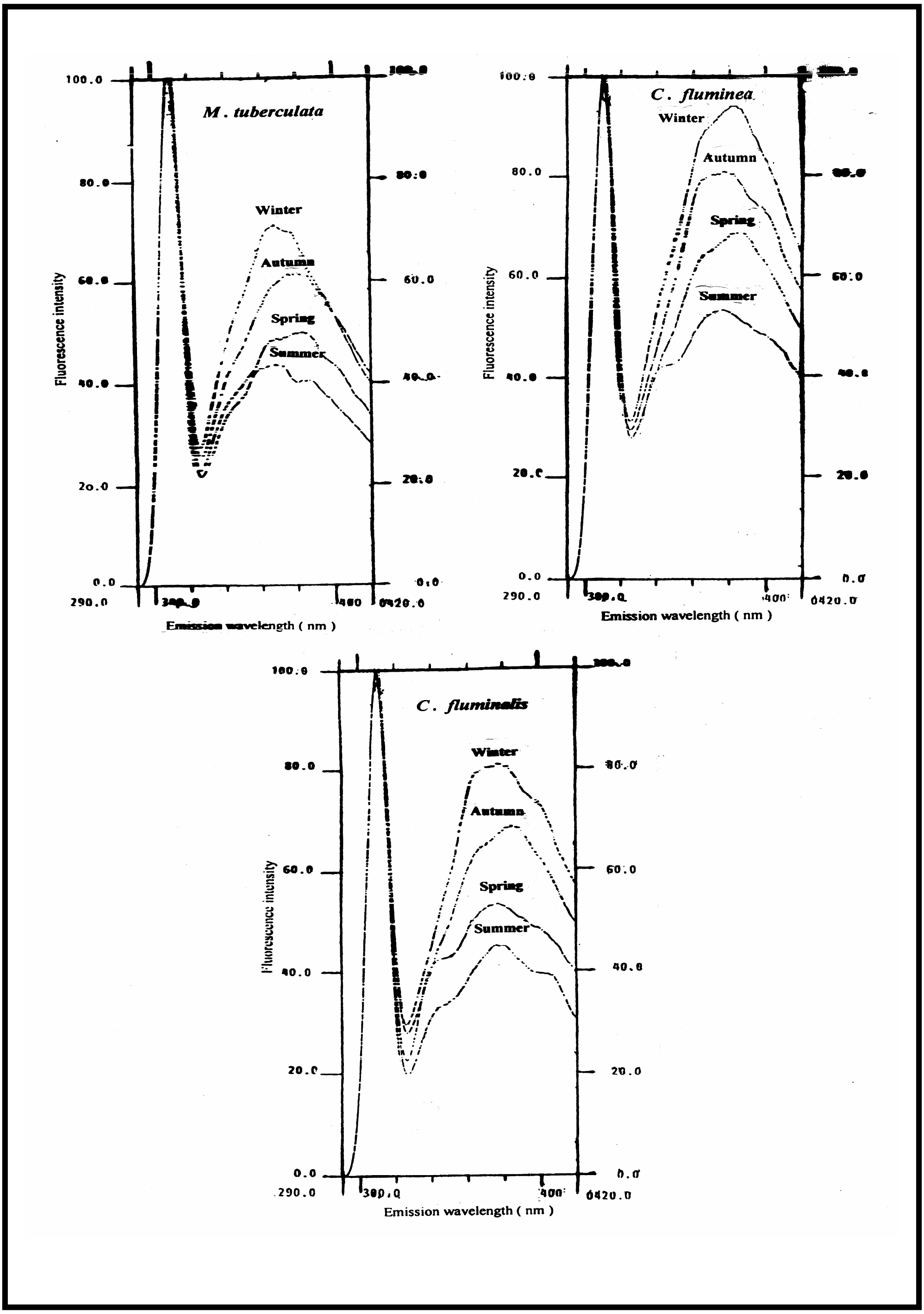

Figure 3. (continued): Fluoresence spectra of total hydrocarbons concentrations in the species of molluscs tissues from Shatt Al-Arab river during 2004- 2005.

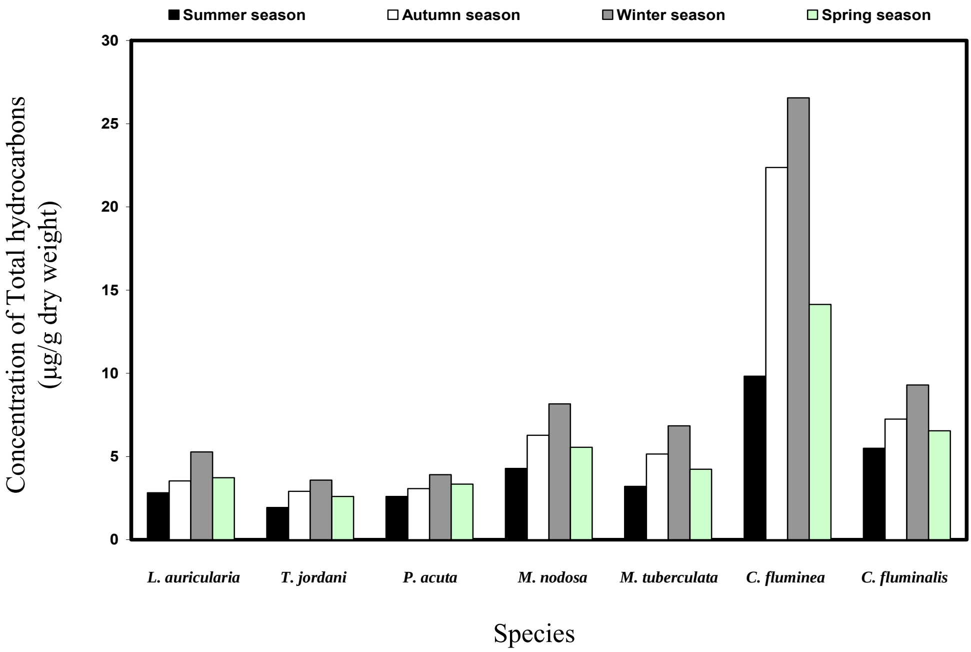

Figure 4. Seasonal variations of total hydrocarbons in species of molluscs from Shatt Al-Arab river during 2004 – 2005.

It was found that the temperature influenced hydrocarbon biodegradation by its effect on the physical nature and chemical composition of oil, rate of microbial metabolism of hydrocarbons and composition of microbial community (Boopathy, 2000). Abdul-Retha (1997) reported that the activity of oil degrading bacteria of Shatt Al-Arab river water was controlled by temperature of water. Shamshoom *et al.* (1990) found that oil degrading bacteria was more active in summer than in winter in Shatt Al-Arab river. The photo-oxidation may also degrade the components of oil in water environment (Ehrhardt and Burns 1993). The intense solar radiations coupled with relatively high water temperature are the characteristic features of the climate of the subtropical regions of Iraq. These two factors could account for rather low levels of hydrocarbons encountered in Shatt Al-Arab river water (Bedair and Al-Saad, 1992; Al-Saad and Al-Timari, 1993; Al-Saad, 1995). Menon and Menon (1995) documented that the hydrocarbons have a tendency to adsorb onto particulate matter. It could be concluded that adsorption of hydrocarbons to Shatt Al–Arab river sediment was the principle mechanism for their removal from water.

Al–Saad (1995) showed pronounced seasonal variations in the average concentrations of hydrocarbons in suspended matter along Shatt Al–Arab estuary being minimum in summer. Accordingly lower concentrations of hydrocarbons in Shatt Al–Arab river water during summer season could be caused in part by the increased sedimentation of adsorbed hydrocarbons. The same conclusion arrived by (DouAbul and Al-Saad, 1985; Al-Saad and Al-Timari, 1993).
The differences in the discharge of hydrocarbons into Shatt Al–Arab river water

during the different seasons could produce seasonal variations in the concentrations of hydrocarbons in the river. Al-Saad (1995) showed that the possible explanation of higher concentrations during winter is that total hydrocarbons discharge was greater than in summer due to the wider occurrence of combustion processes during the cold season as well as the higher association of these hydrocarbons with atmospheric particles at lower ambient temperature. Furthermore, the hydrocarbons deposited on land during summer would not reach the aquatic environment in the same extent as during winter when runoff from land is much more due to rain-storms in the region. Accordingly, one expects that the levels of hydrocarbons that accumulated in the tissues of Shatt Al–Arab river organisms (include molluscs) will be considerably less in summer and spring than in Winter and Autumn.

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التغيرات الفصلية وتوزيع الهيدروكربونات في النواعم المتواجدة في نهر شط العرب

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المستلخص تم دراسة التغيرات الموسمية للهيدروكاربونات في نواعم نهر شط العرب وتشمل النواعم خمسة أنواع من القواقع (*Lymnaea auricularia* و*Theodoxus jordani* و*Physa acuta* و *Melanopsis nodosa* و*Melanoides tuberculata*) ونوعين من المحار (*Corbicula fluminea* و*Corbicula fluminalis*). جمعت عينات النواعم من مناطق مختلفة من نهر شط العرب (على طول المنطقة الممتدة من أبو الخصيب إلى كرمة علي) خلال عام 2004 - 2005. كل نوع من النواعم يتكون على الأقل من 3500 من الأفراد البالغة المتشابه بالحجم. استخلصت الهايدروكاربونات من هذه العينات و قيست بواسطة جهاز التفلور. تراوح تركيز الهايدروكاربونات الكلية (مكافئ لنفط خام البصرة الاعتيادي) في نواعم نهر شط العرب من 1.93 مايكغم/غم وزن جاف في قوقع *T. jordani* إلى 9.83 مايكغم/غم وزن جاف في محار *C. fluminea* خلال فصل الصيف ومن 2.90 مايكغم/غم وزن جاف إلى 22.37 مايكغم/غم وزن جاف خلال فصل الخريف ومن 3.58 مايكغم/غم وزن جاف إلى 26.56 مايكغم/غم وزن جاف خلال فصل الشتاء ومن 2.60 مايكغم/غم وزن جاف إلى 14.13 مايكغم/غم وزن جاف خلال فصل الربيع. بينت الدراسة الحالية بان هناك تغير فصلي بارز في تراكيز الهايدروكربونات في نواعم نهر شط العرب. إذ كان أوطئ تركيز للهيدروكربونات في فصلي الصيف والربيع وأعلى تركيز في فصلي الشتاء والخريف وتعزى التغيرات الموسمية في تراكيز الهايدروكربونات في نواعم نهر شط العرب إلى عوامل بيئية مختلفة.