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Regional and Seasonal Variation of Polycyclic Aromatic Hydrocarbons in Water and Mollusca at Quarna North of Shatt AL-Arab River

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Abstract
Distribution and seasonal variations and sources of of the sixteen polycyclic aromatic hydrocarbons (PAHs) was studied in surface water and and fuor species of molluscs (*Theodoxus Jordani*, *Melanoides taberculata Melanopsis nodosa, Bellamya bengalensis*) from three stations at Al-Quarna in Shatt Al Arab river during the low tide period from September, 2018 to March, 2019 . Liquid-liquid extraction was used for water samples, while PAHs in molluscs were extracted using Soxhlet Extraction and finally analyzed by means of gas chromatography. physical and chemical parameter were measured such as . Water Temperature range from (13°C to 39°C), Dissolved oxygen range from (6.5 mg/l to 3.84 mg/l),PH range from (8.15-7.17) and Electrical conductivity (2.59 ms/cm- 4.75 ms/cm). Results of PAHs in water samples was ranged from (1.4754ng / l) during summer in the first station to (3.4215ng / l) during winter at the third station. While the total PAHs in molluscs range from 0.876 ng/g dry weight in the *T.jordani* in station 1during summer to 9.093 ng/g dry weight in the B.bengalensis during winter . The Highest concentration of PAHs in the four species were arranged as fellow :*Bellamya bengalensis* > *Melanopsis nodosa* > *Melanoides taberculata* > *Theodoxus Jordani.* When we compares the concentration TPHs in water and molluscs with other study it allies within these concentration.
Keywords: PAH, water, Mollusca, Pollution,Qurna,ShattAL-Arab River,Basrah,Iraq
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Introduction

The condition and health of the aquatic environment is constantly being monitored so that the effects of pollution can be better understood and its impact reduced (1). The extent of contamination can be assessed by measuring pollutant concentrations in water, sediments and organic tissue samples. Although easier to process ,water samples are difficult to interpret since the water is constantly flowing, transporting pollutants from one place to another while diluting them, often to concentrations below detection limits (2). One of the most dangerous pollutant for water environment is petroleum hydrocarbons and it's derivatives (3).only limited information is available on the fate of hydrocarbons in the Shatt Al-Arab river. An important route is the uptake and assimilation of these compounds by aquatic organisms in general and mollusca in particular(4). Molluscs are well known for their ability to accumulate hydrocarbons (and other pollutants) and have been employed as indicators of petroleum contamination in many parts of the world (5). Among petroleum hydrocarbon pollutants sixteen polycyclic aromatic hydrocarbons (PAHs) are listed as priority pollutants due to high stability in the environment (6,7). Polycyclic aromatic hydrocarbons (PAHs),having two or more fused benzene rings, are a group of organic pollutants that occur widely in the environment (8) .

There are two origins of PAHs in the environment, natural and anthropogenic.The natural origin attributes to forest fires and volcanic activity, etc. (PAH background values). The anthropogenic one includes incomplete combustion of fossil fuels, and industrial emissions (PAH contamination levels) (9, 10). Aquatic environments are also polluted with PAHs through anthropogenic activities such as accidental oil spills, discharge from routine tanker operations, and municipal and urban runoff. Additionally they tend to accumulate preferentially in river and marine sediments rather than in air or water, due to their high hydrophobicity (11). Generally, PAHs are hydrophobic with very little solubility in water which decreases with increasing molecular weight or the number of fused aromatic rings. The high molecular weight (HMW) PAHs (≥ 4 fused aromatic rings) are less water-soluble, less volatile and more lipophilic than lower molecular weight (LMW) PAHs (≤ 3 fused aromatic rings) (12, 13,14) Due to their carcinogenic and mutagenic effects to both terrestrial and aquatic organisms, PAHs have attracted much attention (15).

Shatt Al-Arab River is the most important river in Iraq, because of its economical , social and ecological values. It is the main source of surface water in Basrah City, southern of Iraq. It's water has been used for various purposes including potable water supply, irrigation, fisheries, navigation, and industrial uses. Moreover, Shatt Al-Arab River is the prime fresh water source and pours about 5x109 m^3 nutrient rich water into the Arabian Gulf each year (16).The Shatt Al-Arab river are known to be severely polluted due to entry of both domestic sewage and industrial wastewater. The industrial effluents are derived from paper and fertilizer mills, electrical power

stations, refined oil plants, petrochemical manufacture and other industries (17).

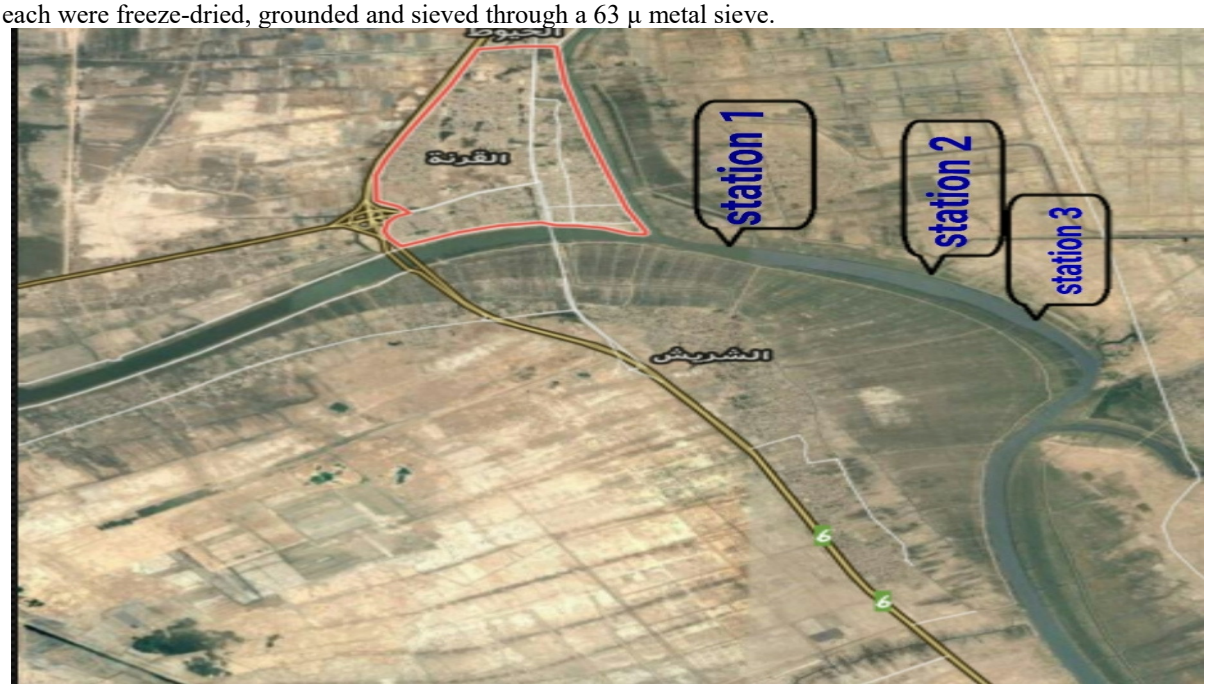
The aims of the present study are to determine the concentrations and source of Polycyclic Aromatic hydrocarbon fractions in water and mollusca, to give baseline data for further work.

Materials and Methods:

Study area and sampling sites:

The confluence of the Tigris and Euphrates rivers at the town of Qurna, north of Basra city forms the Shatt Al-Arab River, which flows to the south west to the Arabian Gulf. The Shatt Al-Arab River has a length of 200 km, a width range between 400 m at Basra and up to more than 2 km at the estuary and a depth of between 8-15 m, considering tides (18 , 19). This study was conducted during the period Spt. 2018 to Mar.,2019. Samples of water and four species of molluscs, *(Theodoxus Jordani*, *Melanoides taberculata Melanopsis nodosa, Bellamya bengalensis)* were collected from the three stations at Quarna in the northern of Shatt al-Arab(Figure 1). Water samples were collected at least 20 -30 cm under the water surface and whenever it was possible at the middle of the river using dark glass bottles and preserved in situ with 25 ml. CCl4. Samples were never taken when it was raining, molluscs Samples were collected at least 350 adult individuals of uniform size of each species.

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 63 µ metal sieve.



(Figure 1) Map of Shatt al-Arab River showing the three sampling stations.

Environmental measurements:

Water physical and chemical parameters including Dissolved oxygen (DO) and Water Temperature (WT), Electrical Conductivity (EC), and pH were measured insitu using the Multimeter type (Multi 350 i SET 5).

Extraction of PAHs from water:

Hydrocarbons in water sample (about 5L) were extracted according to (20) by mixing with another (25 ml) CCl4 for 20 min. using Water Mixer, the liquid fraction was drained , and the residual (about 1L) was transferred into separator funnel . The organic (lower) phase was carefully poured into a glass column containing (5g) of anhydrous sodium sulfate (Na2SO4) ,collected and dried . The residual was dissolved with n-hexane (25 ml) , and passed through a 20 cm glass column (packed with glass wool at the bottom , about 10 g deactivated silica gel (100-200 mesh), 10 g deactivated alumina (100-200 mesh) , and 5g anhydrous sodium sulfate (Na2SO4) at the top). The aromatics were eluted with benzene (25 ml) .The samples dried and stored until detection with Gas-liquid chromatography (for Polycyclic aromatic hydrocarbons (PAHs) .

Helium used as carrier gas in liquid Gas Chromatography with linear velocity of 1 ml./min and Flam Ionization Detector(FID) the operating temperatures for injector and detector were 300^{o}C and 320^{o}C , respectively , and the column temperature was held at 50^{o}C as initial temperature for 8 min. then 8^{o}C/min to350^{o} C.

Extraction of PAHs from molluscs tissues:

The procedure of (21) was used in the extraction of hydrocarbons from molluscs tissues. Ten grams of dried

molluscs tissues were placed in a pre-extracted cellulose thimble and soxhlet extracted with 150 ml 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 sample is taken from the rotator and then placed on a chromatography column that contains the activated silicagel (2% deactivated alumina) to remove the fatty acid residue and a layer of anhydrous sodium sulphate to absorb the water, if any, (50) ml of benzene to obtain the aromatic fraction that evaporates to the extent of dehydration and then dissolved in (5) ml of hexane for the purpose of measuring the total concentration of aromatic hydrocarbons.

The procedure used by (22) was employed to determine the fat content of molluscs samples. Three grams of each freeze- dried sample was soxhlet extracted with a 2 : 1 mixture of petroleum ether and acetone for 24-hours. The extracts were reduced in volume in a rotary vacuum evaporator, and subsequently reduced to exactly 1 ml. Ten µl of the concentrated extracts were taken by a Hamilton syringe and weighted after evaporation of the solvent.

Results and Discussion:

Environmental parameters

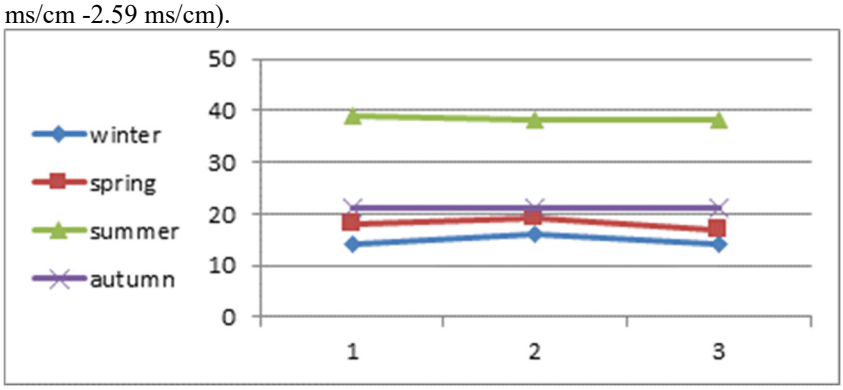
The hydrological condition of the Shatt Al-Arab River basin is affected by several factors including conditions at the upper reaches of the Tigris and Euphrates rivers, the status of advancing flood tides from the Arabian Gulf, seepage of saline ground water into the basin, as well as the impact of climate conditions prevailing in the region on discharge rates and the payload of the river (23).

The basic statistical seasonal variations for the water quality parameters are summarized in Table 1 and illustrated in Figure 2,3 ,4 and 5. Temperature is a high-fluctuations environmental factor, which consider important parameter which regulated the biogeochemical processes in ecosystem (24).Temperature affects the solubility and, consequently, the availability of gases such as oxygen in water (25). it also affects the toxicity of some chemicals in water systems as well as the sensitivity of living organisms to toxic substances(26). In this study, the variability in temperature values at the study locations may have resulted from the weather condition at the time of study (13°C to 39°C).

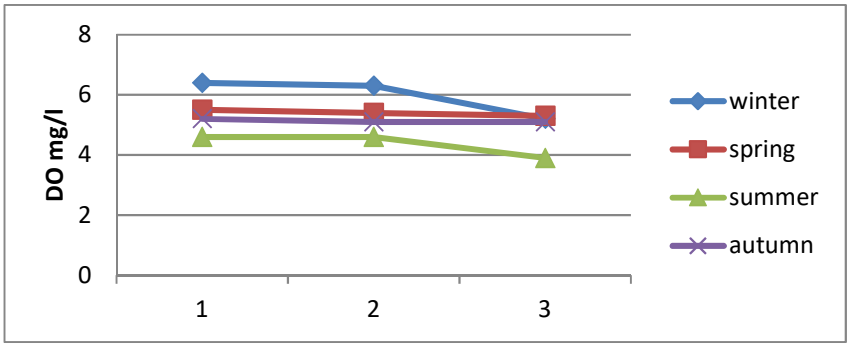
Shatt Al-Arab river has high values of dissolved oxygen due to continuous diffusion , mixing , and the role of phytoplankton , and occurrence of different aquatic plants,The dissolved oxygen is essential for aquatic life, as it is needed to keep organisms alive.The DO content of water is influenced by the sources, raw water temperature and chemical or biological processes taking place in the aquatic system (27) .Our results showed that the DO concentrations range from (6.5 mg/l to 3.84 mg/l).

pH is an important factor to describing the chemical processes state in water, PH mean is a measure the concentration of hydrogen ion (H+) in water(28) The pH results show seasonal differences but for all. Stations fall within the acceptable range of (8.15-7.17); the average values tend to be slightly alkaline during the study period which is consistent with previous studies made on aquatic ecosystems in Southern Iraq(27, 29). The pH is an important parameter that determines the suitability of water for different purposes.

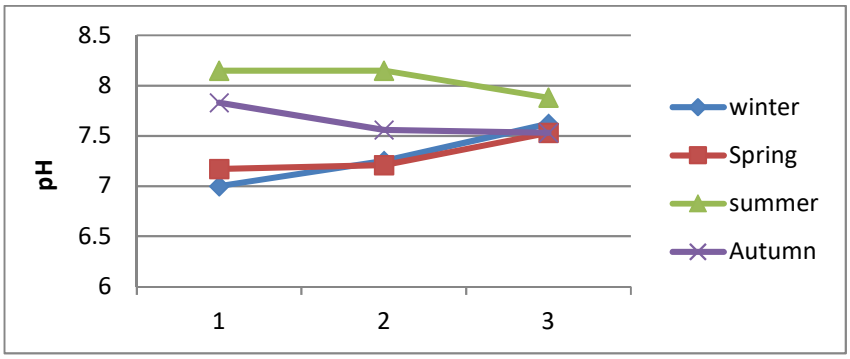
EC estimates the amount of total solids or amount of total dissolved ions in water. The EC of water generally increases as the levels of dissolved pollutants and salinity increases(30). In this study, EC showed clear seasonal differences (4.75 ms/cm -2.59 ms/cm).



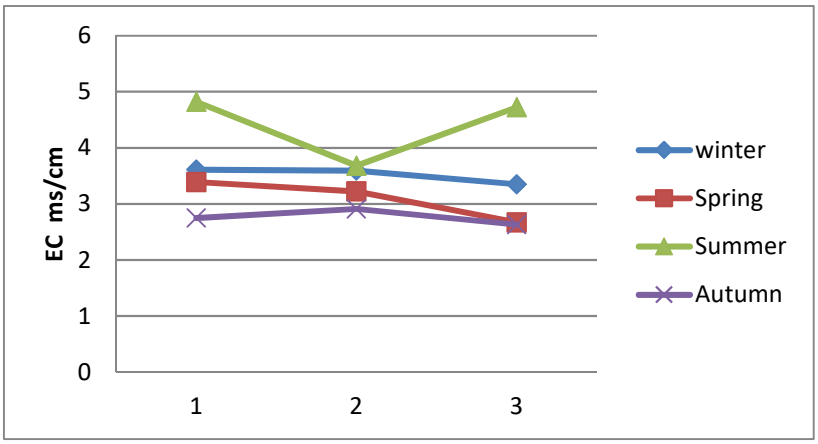
(Fig.2) Water temperatures (°C) at the studied stations



(Fig.3) Dissolved Oxygen (DO) concentrations (mg/l) at the studied stations



(Fig.4) Seasonal variation of (pH) at the studied stations



(Fig.5) Electrical Conductivity(EC ms/cm) at the studied stations

Table (1) Environmental measurements of the three stations during different seasons.

	Station 1		Station 2		Station 3		Season
Parameters	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	
PH	(7.15-7.16)	7- 0.005	(7.21--7.32)	7.25- 0.06	(7.55--7.71)	7.62-0.08	**Winter**
EC	(3.55-3.69)	3.61 -0.07	(3.55-3.66)	3.59-0.06	(3.28-3.46)	3.35-0.094	
DO	(6.3-6.5)	6.4 -0.1	(6.3-6.4)	6.3-0.057	(5.1-5.3)	5.2-0.1	
Water Temp.	(14-15)	14 -0.57	(15-16)	16-0.57	(13-15)	14-1	
PH	(7.17-7.18)	7.17-0.005	(7.10--7.28)	7.21-0.101	(7.47--7.56)	7.53-0.058	**Spring**
EC	(3.32-3.44)	3.39-0.062	(3.21-3.24)	3.22-0.015	(2.61-2.73)	2.67-0.061	
DO	(5.4-5.6)	5.5-0.1	(5.4-5.5)	5.4-0.057	(5.2-5.4)	5.3-0.1	
Water Temp.	(17-19)	18-1	(18-20)	19-1	(17-18)	17-0.577	
PH	(8.14--8.16)	8.15 -0.01	(8.15--8.16)	8.15-0.005	(7.89--7.98)	7.88-0.095	**Summer**
EC	(4.75-4.88)	4.82 -0.066	(3.64-3.76)	3.68-0.066	(4.67-4.76)	4.72-0.049	
DO	(4.6-4.7)	4.6 -0.057	(4.5-4.7)	4.6-0.1	(3.84-3.98)	3.9-0.07	
Water Temp.	(38-39)	39 -0.577	(38-39)	38 -0.577	(37-38)	38-0.577	
PH	(7.83--7.84)	7.83 -0.005	(7.53--7.63)	7.56-0.055	(7.43--7.63)	7.53-0.1	**Autumn**
EC	(2.69-2.85)	2.75 -0.085	(2.89-2.93)	2.91-0.020	(2.59-2.69)	2.63-0.051	
DO	(5.1-5.3)	5.2 -0.1	(5.0-5.2)	5.1-0.115	(5.1-5.4)	5.2-0.152	
Water Temp.	(21-22)	21 -0.577	(20-22)	21-1	(21-22)	21-0.577	

PAH concentration

PAHs do not usually exist as separate entities in environmental media; they are often regarded as a mixture and the total concentration of their mixture is often used to describe their distribution (31). 16 PAHs recommended by the (US EPA) were investigated, The results of the chromatographic gas system showed that concentrations ranged from (1.4754ng / l) in the summer in the first station to (3.4215ng / l) in winter at the third station(table 2,3,4 and Fig.6). The results showed that the total concentrations of PAHs introduced into the environment are higher in winter than in summer This is confirmed by (22) and (32) explained that the increase in the total concentration of PAHs in autumn and winter is due to the fact that aromatic compounds entering the environment are higher in autumn and winter due to the increase in fuel and wood burning, which is used in heating during the winter. As well as the low rate of evaporation of PAHs in the winter and reduce the effectiveness of various microorganisms in the degradation of these compounds with low temperatures (33). While low concentrations in the spring and summer are due to the warm climate of Iraq in summer, where high temperatures cause PAHs to evaporate from water(34) .High temperatures also encourage microorganisms to break down these compounds, especially low molecular weights (35) The process of oxidation is due to the long period of solar brightness and also because of the intensity of solar radiation (33).

Generally, the high molecular weight (HMW) PAHs with ≥4 rings was predominant in the rivers samples . This may be attributed to their low solubility in water, less volatility due to their molecular size and higher persistence in aqueous environment when compared to the low molecular weight (LMW) PAHs (36). The major source of HMW PAHs can be linked to anthropogenic activities(37). HMW PAHs are more persistent than LMW PAHs in the environment due to their increased resistance to oxidation, reduction and vapourisation as molecular weight increases (38). LMW PAHs such as naphthalene and fluorene have more significant acute toxicity to aquatic organisms than HMW PAHs but are non-carcinogenic(31). Some HMW PAHs such as benzo[a]pyrene and benzo[b] fluoranthene are carcinogenic and mutagenic to a wide variety of organisms including fish, birds and mammals(39).

Table (2) the concentrations of PAHs (ng / l) in water in the study area during the year for the first station.

Compounds	Summer	Autumn	Winter	Spring
Naphtalene	_	_	_	_
2-methyl naphthalene	_	_	_	_
1-methyl naphthalene	_	_	0.1975	_
Acenaphthlene	_	_	_	_
Acenaphthene	_	_	0.0314	0.1975
Fluorene	_	0.0594	0.1503	0.0684
Phenanthrene	_	0.0727	0.0533	0.0654
Anthracene	_	0.5215	0.1917	0.0987
Fluoranthene	0.0678	0.0721	0.0317	0.0957
Pyrene	0.6892	0.0862	0.207	0.1342
Benzo[a]fluoranthene	0.0964	0.018	0.0465	0.2451
Chrysene	0.0502	0.4575	1.0383	0.0958
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	0.0392	0.0667	0.0998	0.3761
Di benz[a]pyrene	0.0392	0.1609	1.0926	0.0618
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.4934	0.4987	0.0733	0.5664
Benzo[g,h,i]perylene	_	0.0651	0.0644	0.0343
Total	1.4754	2.0788	3.2778	2.0394
LPAHs	_	0.6536	0.6242	0.43
HPAHs	1.4754	1.4252	2.6536	1.6094
L/H	_	0.458	0.235	0.267
Fl/Py	0.098	0.836	0.153	0.713
Phenanthrene/ Anthracene	_	0.139	0.278	0.662

Table (3) the concentrations of PAHs (ng / l) in water in the study area during the year for the second station.

Compound	Summr	Autumn	Winter	Spring
Naphtalene	_	_	0.0701	_
2-methyl naphthalene	_	_	_	_
1-methyl naphthalene	_	_	0.2475	0.6921
Acenaphthlene	0.0148	0.0821	_	_
Acenaphthene	_	_	0.0546	0.1526
Fluorene	0.0961	0.0904	0.2034	0.0745
Phenanthrene	_	0.0287	_	0.0952
Anthracene	_	0.4015	0.4973	0.0837
Fluoranthene	0.0568	_	0.0578	_
Pyrene	0.0992	0.0652	0.0772	0.3412
Benzo[a]fluoranthene	_	0.0108	0.0667	0.1914
Chrysene	0.0232	0.5873	_	_
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	0.0692	0.0678	0.0908	0.2641
Di benz[a]pyrene	0.0902	0.1409	1.4427	0.0908
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.0845	0.4748	0.3033	0.6624
Benzo[g,h,i]perylene	0.5681	0.0991	0.2542	_
Total	1.1131	2.0486	3.3656	2.648
LPAHs	0.1109	0.6027	1.0729	1.0981
HPAHs	0.9912	1.4459	2.2927	1.5499
L/H	0.111	0.416	0.467	0.708
Fl/Py	0.572	_	0.748	_
Phenanthrene/ Anthracene	_	0.071	_	1.137

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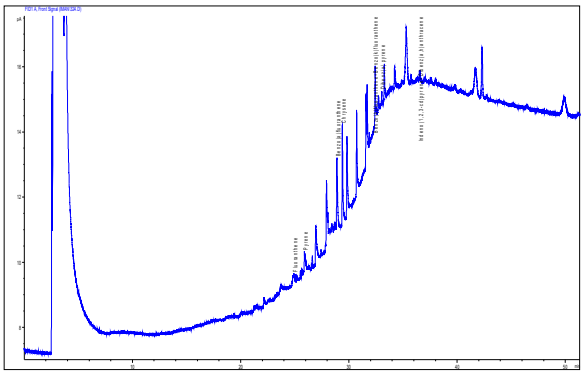
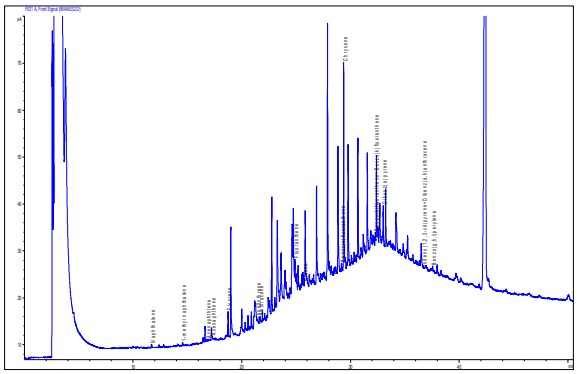
Table (4) the concentrations of PAHs (ng / l) in water in the study area during the year for the third station.

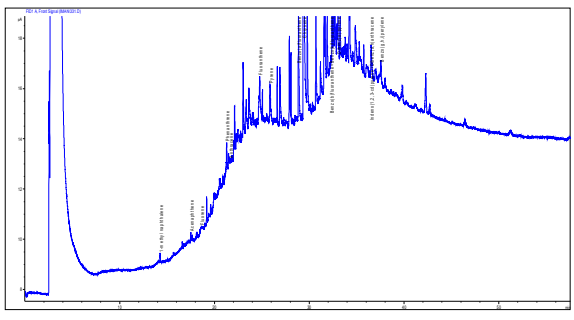
Compound	Summer	Autumn	Winter	Spring
Naphtalene				
2-methyl naphthalene				
1-methyl naphthalene			0.9752	0.9135
Acenaphthlene				0.0367
Acenaphthene			0.1565	
Fluorene	0.1591	0.0444		0.0741
Phenanthrene	0.0858			
Anthracene		0.4015	0.3431	0.0787
Fluoranthene		0.0347	0.0752	0.0925
Pyrene	0.0382		0.0782	0.2041
Benzo[a]fluoranthene		0.1589	0.1447	0.3044
Chrysene	0.1092	0.4743	0.0931	0.0783
Benzo[b]fluoranthene+Benzo[k]Fluoranthene		0.2078		
Di benz[a]pyrene	0.2372	0.2589	1.0297	0.1983
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.1992	0.3081	0.3356	0.7349
Benzo[g,h,i]perylene	0.4989	0.1219	0.1902	0.0921
Total	1.3276	2.0105	3.4215	2.8076
LPAHs	0.2449	0.4459	1.4748	1.103
HPAHs	1.0827	1.5646	1.9467	1.7046
L/H	0.226	0.284	0.757	0.647
Fl/Py			0.961	0.453
Phenanthrene/Anthracene				



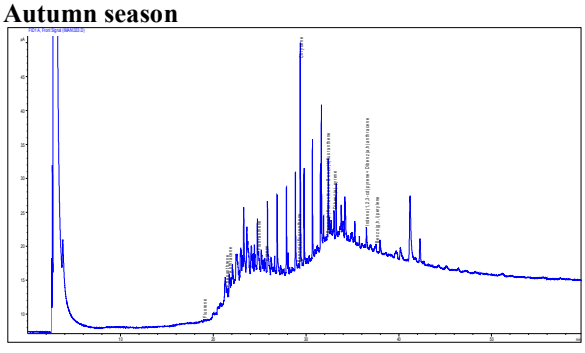
Summer season



Autumn season



Winter season



Spring season

(Fig.6) :Chromatograms of PAHs compounds in water samples of the studied stations during the season

While the concentration in molluscs varied from 3.672 ng /g at the third station in the summer to 7.257ng / g at the first station in the winter in the *M.nodosa* and from 0.876 ng/g in the summer at the first station to 3.506ng/g in the third station in the winter in the *T.jordani* and from 1.778ng / g at the third station in the summer to 5.924ng / g at the second station in the winter in the *M.tuberculata* and from 4.07 ng/g in the summer at the second station to9.093 ng/g at the second station in the winter(table 6,7,8 and fig 7)

The current results showed that the concentrations of PAHs in the water column were lower than those in the

molluscs. This may be the result of optical oxidation and the deposition of PAHs from the water column, making PAHs with low molecular weight predominant in surface water while the higher molecular weight compounds predominated in the molluscs

Sources of PAHs

The sources of PAHs can either be petrogenic i.e., released from petroleum products or pyrogenic due to the combustion of biomass. Diagnostic ratios have been designed and used to distinguish the sources of PAHs due to their stability, physical and chemical attributes (31). Table 2,3 and 4 shows the diagnostic ratios of the PAHs obtained in this study and their possible sources in the water. The ratio of LPAHs/HPAHs in Shatt Al-Arab river were >1 in all station and sesonal which implies that the source of the PAHs was from pyrogenic derived from incomplete combustion of fuel at all stations.

The ratio(fluoranthene/ Pyrene) was less than one at the first station and for all seasons, Either in the second and third stations The(FI/Py) ratio was disadvantage because most water sample had undetectable fluoranthene value and the other samples had undetectable Pyrene values ,only few sample had fluoranthene and Pyrene values together, because that the ratio ranged from 0.5 to 0.9 and indicate the source of PAHs was Petrogenic. Also, the(Phenanthrene/ Anthracene) ratio was disadvantage because most water sample had undetectable Phenanthrene value and the other samples had undetectable Anthracene values ,only few sample had Phenanthrene and Anthracene values together, because that the ratio ranged from 0.139 to 1.13 and indicate the source of PAHs was pyrogenic.This study illustrates the defect of these two indicators in water samples because most samples have undetectable values.

Table 5,6 and 7 shows the diagnostic ratios of the PAHs obtained in this study and their possible sources in the molluscs. The ratio of LPAHs/HPAHs in *M.nodosa* were >1 in all station and seasonal which implies that the source of the PAHs was from pyrogenic derived from incomplete combustion of fuel at all stations. The ratio(fluoranthene/ Pyrene) was more than one at all station and for all seasons, except in the third station in the winter was less than (1) The ratio of (Phenanthrene / Anthracene) is less than the number (10) in all station and seasons and this indicates that the origin of PAHs in snail samples M.nodosa is Petrogenic and Pyrogenic.

The ratio of LPAHs/HPAHs in *T.jordani* were >1 in all station and seasonal , except In the first station in the summer and autumn, the ratio was less than 1. This shows that the origin of PAHs is Petrogenic and a low amount of Pyrogenic. The ratio(fluoranthene/ Pyrene) was more than one at all station and for all seasons, except in the first station in the winter and spring was less than (1) The ratio of (Phenanthrene / Anthracene) is less than the number (10) in all station and seasons and this indicates that the origin of PAHs in snail samples T.jordani is Petrogenic and Pyrogenic (table 8,9 and 10)

The ratio of LPAHs/HPAHs in *M.tuberculata* were >1 in all station and seasonal which implies that the source of the PAHs was from pyrogenic derived from incomplete combustion of fuel at all stations. The ratio(fluoranthene/ Pyrene) was more than one at all station and for all seasons and The ratio of (Phenanthrene / Anthracene) is less than the number (10) in all station and seasons and this indicates that the origin of PAHs in snail samples M.tuberculata is Petrogenic and Pyrogenic(table 11,12and 13)

(Table 14,15 and16) shows The ratio of LPAHs/HPAHs in *B.bengalensis* were >1 in all station and seasonal ,except In the third station in the spring , the ratio was less than (1)This shows that the origin of PAHs is Petrogenic and a low amount of Pyrogenic. The ratio(fluoranthene/ Pyrene) was more than one at all station and for all seasons، except In the first station in the summer This shows that the origin of PAHs is Petrogenic and a low amount of Pyrogenic. and The ratio of (Phenanthrene / Anthracene) is less than the number (10) in all station and seasons and this indicates that the origin of PAHs in snail samples B.bengalensis is Petrogenic and Pyrogenic

Table (5) the concentrations of PAHs (ng / l) in *M.nodosa* in the study area during the year for the first station.

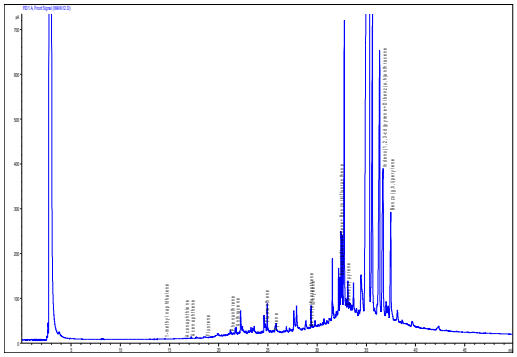
M.nodosa				
Compound	summer	Autumn	Winter	Spring
Naphtalene	_	_	_	_
2-methyl naphthalene	_	_	0.561	0.566
1-methyl naphthalene	0.378	0.421	1.399	0.542
Acenaphthylene	0.361	0.541	0.703	0.499
Acenaphthene	0.267	0.343	0.585	0.456
Fluorene	0.199	0.445	0.489	0.411
Phenanthrene	0.491	0.389	0.632	0.374
Anthracene	0.376	0.363	0.591	0.266
Fluoranthene	0.342	0.254	0.392	0.374
Pyrene	0.232	0.209	0.265	0.246
Benzo[a]fluoranthene	0.179	0.257	0.291	0.271
Chrysene	0.249	0.187	0.238	0.208
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	0.267	0.261	0.256	0.177
Di benz[a]pyrene	0.311	0.256	0.189	0.162
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.166	0.141	0.098	0.121
Benzo[g,h,i]perylene	0.104	0.129	0.094	0.153
Total	3.922	4.196	6.783	4.826
LPAHs	2.072	2.502	4.96	3.114
HPAHs	1.85	1.694	1.823	1.712
L/H	1.12	1.476	2.72	1.818
Fl/Py	1.474	1.215	1.479	1.520
Phenanthrene/ Anthracene	1.305	1.071	1.069	1.406

Table (6) the concentrations of PAHs (ng / l) in *M.nodosa* in the study area during the year for the second station.

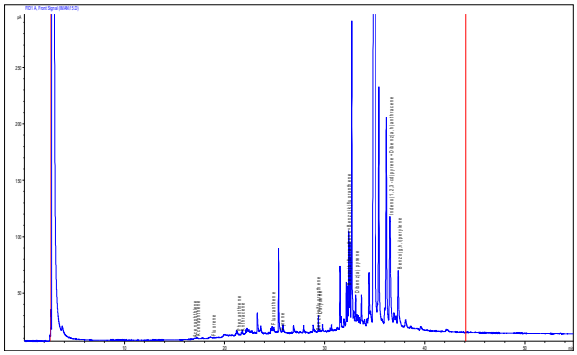
M.nodosa				
Compound	summer	Autumn	Winter	Spring
Naphtalene	_	_	_	_
2-methyl naphthalene	_	0.412	0.583	_
1-methyl naphthalene	0.401	0.436	0.713	0.584
Acenaphthylene	0.396	0.568	1.291	0.521
Acenaphthene	0.372	0.367	0.554	0.467
Fluorene	0.202	0.459	0.495	0.416
Phenanthrene	0.521	0.419	0.663	0.464
Anthracene	0.399	0.391	0.604	0.346
Fluoranthene	0.362	0.321	0.665	0.461
Pyrene	0.284	0.304	0.412	0.363
Benzo[a]fluoranthene	0.239	0.277	0.331	0.271
Chrysene	0.249	0.289	0.338	0.268
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	0.277	0.291	0.269	0.199
Di benz[a]pyrene	_	_	0.211	0.261
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.215	_	0.128	0.222
Benzo[g,h,i]perylene	_	_	_	_
Total	3.917	4.534	7.257	4.843
LPAHs	2.291	3.052	4.903	2.798
HPAHs	1.626	1.482	2.354	2.045
L/H	1.408	2.059	2.082	1.368
Fl/Py	1.274	1.055	1.614	1.269
Phenanthrene/ Anthracene	1.305	1.071	1.097	1.341

Table (7) the concentrations of PAHs (ng / l) in *M.nodosa* in the study area during the year for the third station.

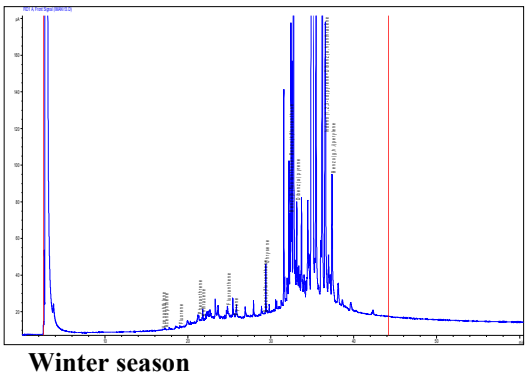
M.nodosa				
Compound	summer	Autumn	Winter	Spring
Naphtalene				
2-methyl naphthalene				
1-methyl naphthalene	0.362	0.368	0.746	
Acenaphthylene	0.349	0.582	1.547	0.545
Acenaphthene	0.412	0.383	0.612	0.578
Fluorene	0.213	0.391	0.521	0.455
Phenanthrene	0.457	0.445	0.695	0.485
Anthracene	0.432	0.296	0.638	0.331
Fluoranthene	0.377	0.365	0.456	0.442
Pyrene	0.344	0.338	0.472	0.384
Benzo[a]fluoranthene	0.139	0.147	0.358	0.294
Chrysene	0.143	0.249	0.369	0.283
Benzo[b]fluoranthene+Benzo[k]Fluoranthene		0.343	0.287	0.209
Di benz[a]pyrene	0.197		0.268	0.396
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.247		0.164	0.267
Benzo[g,h,i]perylene				
Total	3.672	3.907	7.133	4.669
LPAHs	2.225	2.465	4.759	2.394
HPAHs	1.447	1.442	2.374	2.275
L/H	1.537	1.709	2.004	1.052
Fl/Py	1.095	1.079	0.966	1.151
Phenanthrene/ Anthracene	1.057	1.503	1.089	1.465



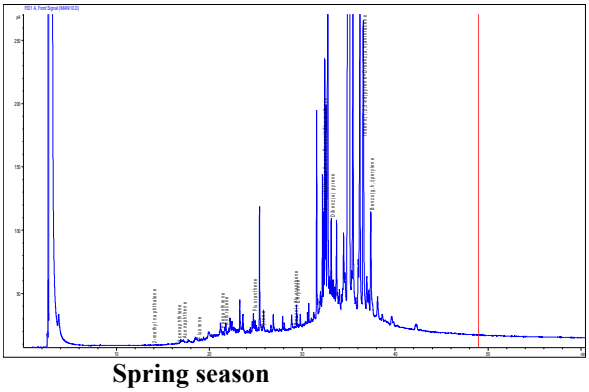
Summer season



Autumn season



Winter season



Spring season

(Fig.7) :Chromatograms of PAHs compounds in *M.nodoas* samples of the studied stations during the season

Table (8) the concentrations of PAHs (ng / l) in *T.jordani* in the study area during the year for the first station.

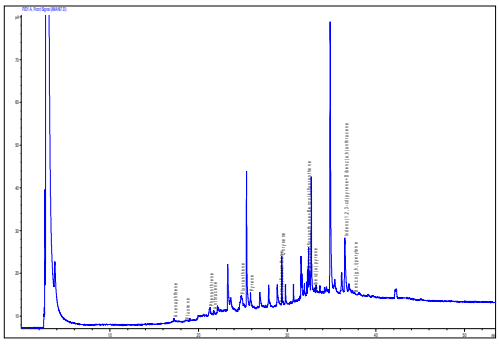
T.jordani				
Compound	summer	Autumn	Winter	Spring
Naphtalene	_	_		_
2-methyl naphthalene	_	_	_	_
1-methyl naphthalene				
Acenaphthlene	0.093	_	0.265	0.127
Acenaphthene	0.099	0.148	0.243	_
Fluorene	0.076	0.152	0.232	0.136
Phenanthrene	0.075	0.166	0.205	0.102
Anthracene	0.063	0.157	0.179	0.115
Fluoranthene	0.068	0.119	0.141	0.034
Pyrene	0.058	0.112	0.137	0.061
Benzo[a]fluoranthene	0.059	0.105	0.176	0.069
Chrysene	0.043	0.081	0.129	0.078
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	0.089	0.079	0.121	0.053
Di benz[a]pyrene	0.056	0.066	0.179	0.071
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.045	0.054	0.081	0.052
Benzo[g,h,i]perylene	0.052	0.061	0.061	0.068
Total	0.876	1.3	2.149	0.966
LPAHs	0.406	0.623	1.124	0.48
HPAHs	0.47	0.677	1.025	0.486
L/H	0.863	0.920	1.096	0.987
Fl/Py	1.172	1.062	1.029	0.55
Phenanthrene/ Anthracene	1.19	1.057	1.145	0.886

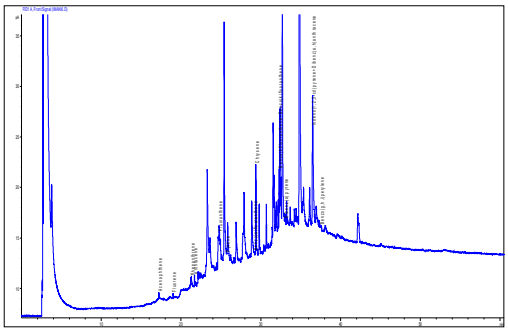
Table (9) the concentrations of PAHs (ng / l) in *T.jordani* in the study area during the year for the second station.

T.jordani				
Compound	summer	Autumn	Winter	Spring
Naphtalene				
2-methyl naphthalene	_	_	_	0.313
1-methyl naphthalene	0.179	0.146	_	_
Acenaphthylene	0.153	0.168	0.304	0.333
Acenaphthene	0.139	0.181	0.356	0.229
Fluorene	0.086	0.162	0.361	0.232
Phenanthrene	0.095	0.106	0.317	0.209
Anthracene	0.082	0.097	0.292	0.155
Fluoranthene	0.074	0.094	0.253	0.135
Pyrene	0.058	0.072	0.247	0.109
Benzo[a]fluoranthene	0.079	0.085	0.256	0.141
Chrysene	0.033	0.121	0.213	0.127
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	_	0.119	0.235	_
Di benz[a]pyrene	0.067	0.106	0.262	_
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.052	0.094	_	0.142
Benzo[g,h,i]perylene	0.048	0.101	_	_
Total	1.145	1.652	3.096	2.125
LPAHs	0.734	0.86	1.63	1.471
HPAHs	0.411	0.792	1.466	0.654
L/H	1.785	1.08	1.111	2.249
Fl/Py	1.275	1.305	1.024	1.238
Phenanthrene/ Anthracene	1.158	1.092	1.085	1.348

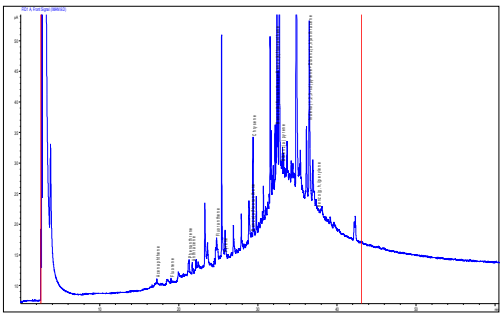
Table (10) the concentrations of PAHs (ng / l) in *T.jordani* in the study area during the year for the third station.

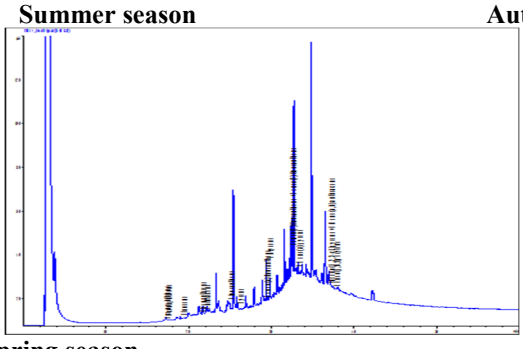
T.jordani				
Compound	summer	Autumn	Winter	Spring
Naphtalene	_	_	_	_
2-methyl naphthalene	_	_	_	_
1-methyl naphthalene	0.135	_	_	_
Acenaphthylene	0.176	0.123	0.454	0.374
Acenaphthene	0.158	0.168	0.467	0.437
Fluorene	0.096	0.145	0.487	0.216
Phenanthrene	0.099	0.117	0.374	0.237
Anthracene	0.079	0.085	0.243	0.132
Fluoranthene	0.074	0.078	0.238	0.235
Pyrene	0.061	0.055	0.271	0.158
Benzo[a]fluoranthene	0.104	0.075	0.262	0.102
Chrysene	0.073	0.066	0.293	0.097
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	_	0.093	0.205	_
Di benz[a]pyrene	0.121	0.111	0.212	_
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.093	0.059	_	0.089
Benzo[g,h,i]perylene	0.048	0.091	_	_
Total	1.317	1.266	3.506	2.077
LPAHs	0.743	0.638	2.025	1.396
HPAHs	0.574	0.628	1.481	0.681
L/H	1.294	1.015	1.367	2.049
Fl/Py	1.213	1.418	0.878	1.487
Phenanthrene/ Anthracene	1.253	1.376	1.539	1.795





Summer season **Autumn season**





Winter season **Spring season**

(Fig.8) :Chromatograms of PAHs compounds in *T.jordani* samples of the studied stations during the season

Table (11) the concentrations of PAHs (ng / l) in *M.tuberculata* in the study area during the year for the first station.

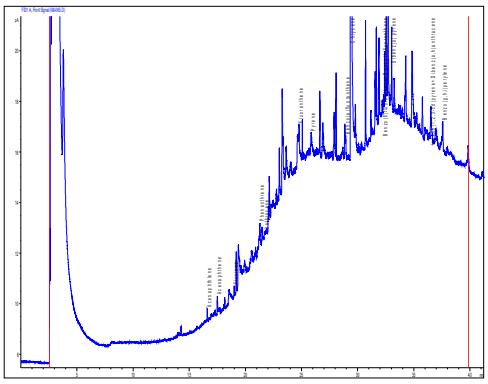
M.tuberculata				
Compound	summer	Autumn	Winter	Spring
Naphtalene				
2-methyl naphthalene	_	_	0.391	_
1-methyl naphthalene	_	_	0.332	_
Acenaphthlene		0.252	1.121	
Acenaphthene	0.169	_	0.266	_
Fluorene	0.188	0.401	0.283	0.426
Phenanthrene	0.238	0.411	0.274	0.346
Anthracene	0.166	0.211	0.221	0.261
Fluoranthene	0.098	0.189	1.216	0.159
Pyrene	0.061	0.176	0.204	0.106
Benzo[a]fluoranthene	0.103	0.109	0.199	0.173
Chrysene	0.111	_	_	0.146
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	0.093	0.112	0.141	0.134
Di benz[a]pyrene	0.115	0.017	0.152	0.115
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.098	0.075	0.128	0.099
Benzo[g,h,i]perylene	0.072	0.097	0.121	0.065
Total	1.512	2.05	5.049	2.03
LPAHs	0.761	1.275	2.888	1.033
HPAHs	0.751	0.775	2.161	0.997
L/H	1.013	1.645	1.336	1.036
Fl/Py	1.606	1.073	5.96	1.5
Phenanthrene/ Anthracene	1.433	1.947	1.239	1.325

Table (12) the concentrations of PAHs (ng / l) in *M.tuberculata* in the study area during the year for the second station.

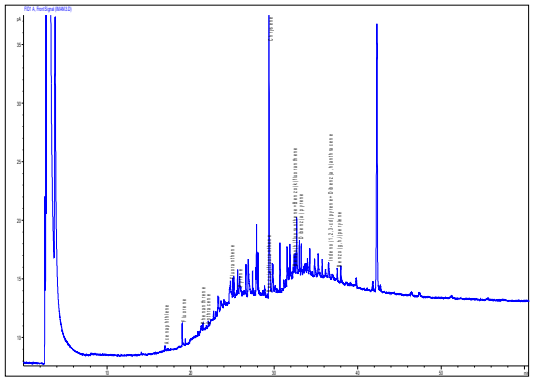
M.tuberculata				
Compound	summer	Autumn	Winter	Spring
Naphtalene	_	_	_	_
2-methyl naphthalene	_	0.295	0.306	_
1-methyl naphthalene	0.169	0.283	0.319	0.153
Acenaphthlene	0.117	0.229	0.223	0.259
Acenaphthene	0.177	0.162	0.326	0.379
Fluorene	0.154	0.352	2.009	0.461
Phenanthrene	0.162	0.341	0.348	0.331
Anthracene	_	0.234	0.251	0.238
Fluoranthene	0.124	0.177	0.461	0.248
Pyrene	0.118	0.164	0.224	0.246
Benzo[a]fluoranthene	0.134		1.003	0.265
Chrysene	0.103	0.193	0.207	0.363
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	_	0.097	0.12	0.141
Di benz[a]pyrene	0.131	0.053	0.127	
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	_	_	_	0.096
Benzo[g,h,i]perylene	_	_	_	0.078
Total	1.389	2.58	5.924	3.258
LPAHs	0.779	1.896	3.782	1.821
HPAHs	0.61	0.684	2.142	1.437
L/H	1.277	2.771	1.765	1.267
Fl/Py	1.05	1.079	2.058	1.008
Phenanthrene/ Anthracene	_	1.457	1.386	1.39

Table (13) the concentrations of PAHs (ng / l) in *M.tuberculata* in the study area during the year for the third station.

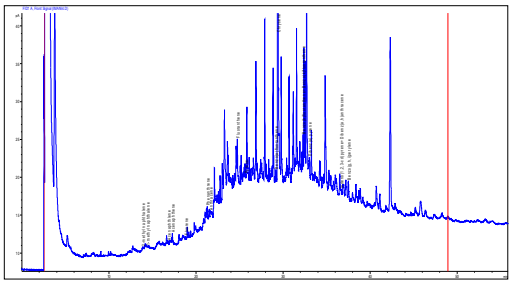
M.tuberculata				
Compound	summer	Autumn	Winter	Spring
Naphtalene				
2-methyl naphthalene	0.124	_	0.216	_
1-methyl naphthalene	0.136	0.134	0.199	0.239
Acenaphthlene	0.107	0.391	0.183	0.206
Acenaphthene	_	0.268	_	0.392
Fluorene	0.232	0.304	0.159	0.373
Phenanthrene	0.198		0.456	0.394
Anthracene	0.157	0.255	0.315	0.181
Fluoranthene	0.124	0.193	0.497	0.283
Pyrene	_	0.134	0.294	0.216
Benzo[a]fluoranthene	0.339	_	1.803	0.259
Chrysene	0.156	0.12	0.672	0.336
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	0.094	0.102	0.116	
Di benz[a]pyrene	_	0.093	0.071	0.135
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.111	0.095	0.068	0.106
Benzo[g,h,i]perylene				
Total	1.778	2.089	5.049	3.12
LPAHs	0.954	1.352	2.362	1.785
HPAHs	0.824	0.737	2.321	1.335
L/H	1.157	1.834	1.017	1.337
Fl/Py	_	1.44	1.69	1.31
Phenanthrene/ Anthracene	1.261	_	1.447	2.176



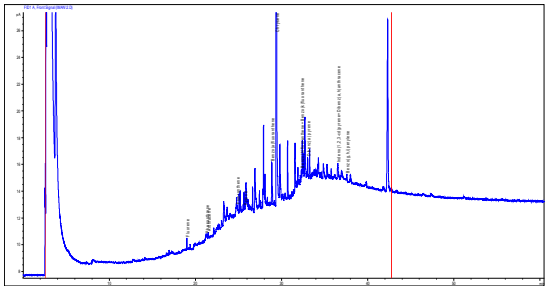
Summer season



Autumn season



Winter season



Spring season

(Fig.9) :Chromatograms of PAHs compounds in *M.tuberculata* samples of the studied stations during the season

Table (14) the concentrations of PAHs (ng / l) in *B.bengalensis* in the study area during the year for the first station.

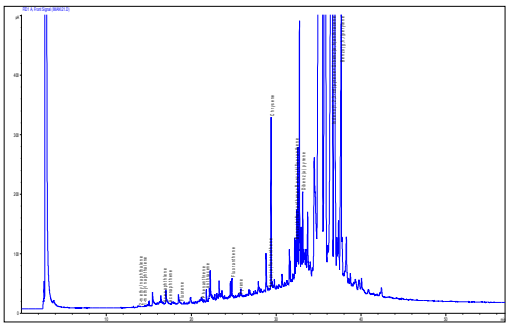
B.bengalensis				
Compound	**Summer**	**Autumn**	**Winter**	**Spring**
Naphtalene		0.365	0.599	
2-methyl naphthalene	0.342	0.297	0.365	0.394
1-methyl naphthalene	0.251	0.263	0.518	0.484
Acenaphthylene	0.427	0.586	0.743	0.476
Acenaphthene	0.412	0.595	0.675	0.602
Fluorene	0.274	0.412	0.697	0.467
Phenanthrene	0.487	0.512	0.523	0.613
Anthracene	0.327	0.414	0.821	0.569
Fluoranthene	0.421	1.034	0.698	0.538
Pyrene	0.561	0.131	0.692	0.509
Benzo[a]fluoranthene	0.297	0.112	0.732	0.633
Chrysene	0.214	0.135	0.675	0.467
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	0.192	0.066	0.723	0.321
Di benz[a]pyrene	0.106	0.055	0.349	0.231
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.117	0.247	0.199	0.247
Benzo[g,h,i]perylene	0.056	0.163	0.084	0.163
Total	4.484	5.387	9.093	6.714
LPAHs	2.52	3.444	4.941	3.605
HPAHs	1.964	1.943	4.152	3.109
L/H	1.283	1.772	1.190	1.159
Fl/Py	0.750	7.893	1.008	1.056
Phenanthrene/ *Anthracene*	1.489	1.236	0.637	1.077

Table (15) the concentrations of PAHs (ng / l) in *B.bengalensis* in the study area during the year for the second station.

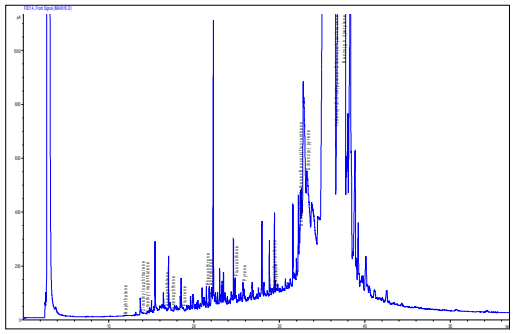
B.bengalensis				
Compound	summer	Autumn	Winter	Spring
Naphtalene	_			_
2-methyl naphthalene	0.452	0.272	0.615	0.461
1-methyl naphthalene	0.366	0.256	0.583	0.378
Acenaphthylene	0.387	0.562	0.943	0.506
Acenaphthene	0.192		0.495	0.629
Fluorene		0.327	1.097	
Phenanthrene	0.517	1.026	0.872	
Anthracene	0.277	0.514	0.518	1.069
Fluoranthene	0.798	0.734	0.958	0.537
Pyrene	0.214	0.347	0.784	0.492
Benzo[a]fluoranthene	0.317	0.402		0.536
Chrysene	0.243	0.325	0.562	0.237
Benzo[b]fluoranthene+Benzo[k]Fluoranthene			0.831	0.611
Di benz[a]pyrene	0.076	0.035	0.449	0.257
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.175	0.147	0.209	0.221
Benzo[g,h,i]perylene	0.056	0.133	0.094	0.132
Total	4.07	5.08	9.01	6.066
LPAHs	2.191	2.957	5.123	3.043
HPAHs	1.879	2.123	3.887	3.023
L/H	1.166	1.392	1.317	1.006
Fl/Py	3.728	2.115	1.221	1.091
Phenanthrene/ *Anthracene*	1.866	1.996	1.683	_

Table (16) the concentrations of PAHs (ng / l) in *B.bengalensis* in the study area during the year for the third station.

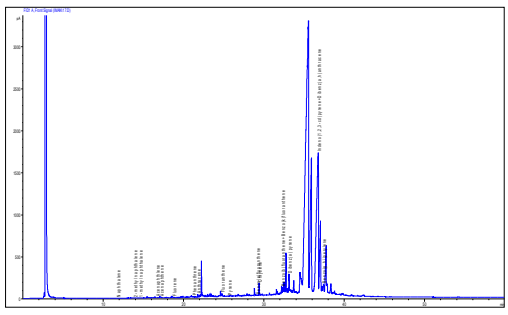
B.bengalensis				
Compound	summer	Autumn	Winter	Spring
Naphtalene	_	_	_	_
2-methyl naphthalene		1.426	_	_
1-methyl naphthalene	0.356	0.567	1.637	0.738
Acenaphthylene	0.476	0.692	0.683	0.566
Acenaphthene	1.042	_	0.686	0.493
Fluorene	_	0.274	0.497	0.265
Phenanthrene	0.678	0.669	0.888	_
Anthracene	0.307	0.544	0.872	0.969
Fluoranthene	0.378	0.373	0.689	0.471
Pyrene	0.341	0.271	0.834	0.328
Benzo[a]fluoranthene	0.379	0.392	_	0.631
Chrysene	0.272	0.325	0.762	0.467
Benzo[b]fluoranthene+Benzo[k]Fluoranthene	0.085	0.124	0.417	0.311
Di benz[a]pyrene	0.091	0.126	0.496	0.275
Indeno[1,2,3-c,d]pyrene+Di benz[a,h]anthracene	0.253	0.152	0.273	0.313
Benzo[g,h,i]perylene	0.076	0.059	0.104	0.423
Total	4.734	5.994	8.838	6.25
LPAHs	2.859	4.172	5.263	3.031
HPAHs	1.875	1.822	3.575	3.219
L/H	1.524	2.289	1.472	0.941
Fl/Py	1.108	1.376	0.826	1.435
Phenanthrene/ *Anthracene*	2.208	1.229	1.018	_



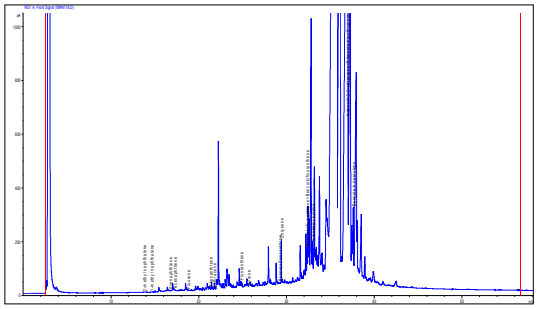
Summer season



Autumn season



Winter season



Spring season

(Fig.9) :Chromatograms of PAHs compounds in *B.bengalensis* samples of the studied stations during the season

Conclusion:

Water and 4 species of Mollusca have some concentrations of Polycyclic Aromatic hydrocarbons.

The Highest concentration of PAHs in the four species were arranged as fellow :*Bellamya bengalensis* > *Melanopsis nodosa* > *Melanoides taberculata* > *Theodoxus Jordani.*

The sources of PAHs came from many sources, and there is seasonal variations of PAHs in the water due to many factor such as Temperature, photooxidation and bacterial degradation.

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