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Original article

Detection of Aromatic Compounds in Some Samples of Shell at Darnh Coast

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ABSTRACT

Background and aims*. Polycyclic aromatic hydrocarbon (PAH) is wide- spread class of environmental chemical pollutants with mutagenic and carcinogenic properties and it can accumulate in different matrices of the aquatic environment. This study was aimed to assess the degree of contamination by PAHs of the coastal sediments in non-industrialized area of Mediterranean Sea.* ***Methods****. The area of study extends along the coast Port Darnh City about 4km in the east of Darnh. Three locations were chosen; Hydrocarbons have been determined in Shell. The samples were analyzed for aromatic hydrocarbons following different steps including; extraction, cleaning up, fractionation, instrumental analysis and analytical quality control.* ***Results****. The results showed that the high contents of PAHs were recorded at AL Port (1,2) location, in the Marine Shell (Monodonta) samples of with values of (10.72 and 10.82 µg/g), respectively, and contents of PAHs in Monodenta shells* were as *following (8.92 µg/g) for the locations of port 3. On the other side the contents of PHAs in the Patella shell samples were fluctuated in the ranges of (4.1 µg/g), (8.08 µg/g) and (9.0 µg/g) at the locations of Port 1,2,3, respectively.* ***Conclusion****. This study has satisfied the hydrocarbons concentration of marine in shell taken from area Al Jabal Al - Akhdar- for port in Darnh city, that most the studied samples containing aromatic hydrocarbons.*

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INTRODUCTION

The aquatic ecosystem is a major subdivision of the biosphere. The Mediterranean Sea is subject to increasing anthropogenic pressure due to the growth of the permanent population on the Mediterranean coast, as much as 200,000 commercial vessels ply the Mediterranean annually ports therein, whereas more than 40 major refineries and petrochemical plants are located in the region [1]. Polycyclic aromatic hydrocarbon (PAH) is wide- spread class of environmental chemical pollutants with mutagenic and carcinogenic properties and it can accumulate in different matrices of the aquatic environment [2,3]. Several studies have shown that PAHs can be transported from polluted areas to remote regions through atmospheric transport, which could occur as a sequence of successive volatilization and condensation processes. In marine environments, these hydrophobic compounds with very low water solubility sorb to particulate organic matter and eventually sink to deep waters and sediments which are the final sink [4].

PAHs are ubiquitous organic compounds that can result from natural processes such as forest fires, volcanic eruption and petroleum products, short-term degradation of biogenic precursors (diagenesis) and anthropogenic sources such as engine exhaust, industrial activities, natural gas, domestic heating system and incinerators that are considered to be the major source to the environment [2]. Elevated concentration of PAHs has been found in dolphins and fin whales of the Mediterranean [5]. Pointing out that the accumulation of this class of pollutants in the Mediterranean food web may be dangerous. Due to their high persistence, long- range transport through both atmosphere and water and their tendency

to accumulate in biota and sediments, they can be considered indicators of anthropogenic pollution [6]. This study was aimed to assess the degree of contamination by PAHs of the coastal sediments in a non-industrialized area of Mediterranean Sea such as the possible sources for these organic contaminants and to investigate the source of much of the contamination or pollution within the location.

METHODS

Description of the study sites

The area of study extends along the coast Port Darnh City about 4 km in the east. Darnh City is situated in eastern Libya, lies on the coast of the East Mediterranean of the coast of Libya. The steepest and most elevated Aljabal *ALakhtar*. Coasts are to be found in this areas, as some limestone coastal formations reach 100 m (*Ras Hilal* and *Lathroon*), with the Green mountain running down to the sea, directly or with a very narrow coastal plain. This area is also relatively richer in coastal headlands **(***Karsa, Ras Hilal* and *Ras Amer,* and *Darnh*). The beaches in this part of the coast vary from narrow sandy beaches to gravelly or rocky boulders in some parts, as a result of sand precipitation in wadi mouths or strong wave action on limestone formations. Three locations were chosen as shown in Figure 1.

Figure 1. Map showing the locations of the study area.

Data collection procedure

Sampling and Shell Marine Determination of Hydrocarbons

Hydrocarbons have been determined in shell according to [7]. The samples were analyzed for aromatic hydrocarbons following different steps including; extraction, cleaning up and fractionation, instrumental analysis and analytical quality control.

Chemical Analysis

Hydrographical Parameters Analysis

Some parameters were totally or partially measured in the field as soon as the samples collected. These steps of the methods would be explained by the term "*in situ*" [8].

Temperature Measurements (°C)

In situ, at each station, air and water temperatures were measured at the time of water sampling to the nearest 0.1 °C by using an ordinary thermometer.

Salinity (S ‰)

Salinity was determined by measuring the electrical conductivity using an inductive Salinometer (Beckman; model RS-10).

Hydrogen-ion concentration (pH)

The pH-value of water sample was measured in the site immediately after collection using Bench type (JEN WAY, 3410 Electrochemistry Analyzer pH-meter).

Oxygen Study (Dissolved Oxygen (DO)
It was determined by using DO meter in the site.

Hydrocarbons Analysis
PAHs analysis (The Polycyclic Aromatic Hydrocarbons), was used well-established techniques [7].

Extraction step of hydrocarbons for Shell
Ten grams of shell were treated with 30 g of anhydrous sodium sulfate and the mixture was blended at high speed for 5 min. Then the mixture was extracted using a soxhlet with 200 ml of methanol for 8 hrs. 20 ml of 0.7 M KOH and 30 ml of distilled water were added to the flask and the reflux was continued for 2 hrs to saponify the lipids. The content of the extraction flask was extracted three times in a separating funnel with 80 ml hexane. The three extracts were combined, dried with anhydrous sodium sulfate and filtered through glass wool. The hexane fraction was concentrated with a rotary evaporator down to about 15 ml at 300C and concentrated down to a volume of 1 ml with nitrogen gas stream and then subjected to cleaning up and fractionation [9].

Cleaning up and fractionation
Cleaning up and fractionation were performed by passing the concentrated extract through a silica/aluminum oxide column. The chromatography column was prepared by slurry packing 20 ml of hexane containing 10 g of silica, followed by 10 ml containing 10 g of aluminum oxide and finally 1 g of anhydrous sodium sulfate. The hydrocarbon sample extract (1 ml) was sequentially eluted from the column with 25 ml of hexane for the saturated aliphatic fraction (F1), and then 60 ml of hexane and dichloromethane (80:20) was used for the elution of the unsaturated aromatic fraction (F2). F1 and F2 were concentrated using gentle stream of nitrogen for instrumental analysis.
2µL of each sample of unsaturated aromatic fraction was injected in the split less mode and purge time was 1 min. the response factor of individual hydrocarbon compounds to the internal standard was measured and calculated at least three times (at the beginning, in the middle, and at the end for each batch of GC injections). Identification and quantification of hydrocarbon compounds were based on matching their retention time with a mixture of hydrocarbon standards [9].

Statistical Analysis
One-way analysis of variance (ANOVA) was used to evaluate the inter-specific significance between shell hydrocarbons accumulation and between hydrocarbons levels in different sites with, Significance was set at < 0.05 using Minitab software version 17.

RESULTS

Hydrographical Parameters
Temperature (°C): The absolute the chapter average values of air and surface water temperature at the different sites during the period February 2023 were given in Table 1. The water temperature (°C) measured in situ exhibited wide variations, which attains its maximum value of 21.2°C in February 2023 in the East Darnh City Water Port 3. While the average values for the studied areas Port 1and Port 2 were 19.4 and 18.9 respectively. It is evident that the surface water temperatures followed that of the air above it and considerably lower than its mean.

Salinity (S‰): The absolute, the regional averages of salinity in the surface water during the year of study were recorded. The average values for the studied areas in February 2023, respectively, fluctuated between (38.0%), (37.6%), (37.5 %). Salinity, as temperature, is one of the most important limiting factors of biological distribution in aquatic environment. It is noticed that variation in salinity during the period of investigation at each station is relatively limited.

Hydrogen Ion Concentration (pH): The pH-values of the surface water at the selected locations in front of the East Darnh beach were measured during the year of study. The pH-values ranged between a minimum of 6.5 and a maximum of 7.2 in study areas.

Dissolved Oxygen (DO): The surface distribution of dissolved oxygen, (ml/L), in the beach waters of East Darnh as well as the corresponding saturation percentages during the year were presented in Table 1. The distribution pattern of DO at the different areas varied from a minimum of (8.9 ml/L) Port 1 to a maximum of (10.0 ml/L) at Port 2 in February 2023, respectively.

Table 2 was presented correlation coefficients between Hydrographical parameters. A good correlation was found between dissolved oxygen (DO) and salinity (S ‰) (R^2 = 0.955) and between pH and DO (R^2 = 0.446), A negative correlation was found between other environmental parameters.

Table 1. Distribution in Percentage of Hydrographical Parameters.

Site / parameters	Temperature **(TC°)**	Salinity **(S ‰)**	Hydrogen **(PH)**	Oxygen **(DO)** (mg/l)
Port 1	19.4	38.0	7.2	9.7
Port 2	18.9	37.6	6.5	10.0
Port 3	21.2	37.5	6.9	8.9
TOTAL	**59.5**	**113.1**	**20.6**	**28.6**

Table 2. correlation coefficients between Hydrographical Parameters.

Environmental parameters	**TCº**	**(S %)**	**DO(mg/l)**	**Ph**
TCº	1			
(S‰)	0.665	1		
DO (mg/l)	-0.432	0.955*	1	
pH	**-0.154**	**0.215**	**0.446**	**1**

HYDROCARBONS

Poly Aromatic Hydrocarbons (PAHS)

Table 3 and Table 4 were illustrated the concentrations (ppm) of aromatic hydrocarbons in the Marine Shell (Monodonta, *Patella*), for three Ports in Darnh City (Port 1, Port 2 and Port 3).

The poly aromatic hydrocarbons which obtainedand detected by GC-Mass instrument in this study including (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo (a) anthracene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Dibenzo (a, h) anthracene, Benzo(ghi) Perylene, andindeno and (1,2,3-cd) Pyrene.

The results showed that the high contents of PAHs were recorded at Port (1 and 2) location in the Marine shell *(Monodonta)* samples with values of (10.72 and 10.82 µg/g), respectively, and contents of PAHs in *Monodenta* shells were as following (8.92 µg/g) for the locations of port 3.

On the other side the contents of PHAs in the *patella* shell samples were fluctuated in the ranges of (4.1 µg/g), (8.08 µg/g) and (9.0 µg/g) at the locations of port 1, 2 and 3 respectively.

Tables 3. show the results of aromatic hydrocarbons in the Marine Shell (Monodonta) samples in three areas (Port 1, Port 2 and Port 3).

Compound	***Shell Monodonta***			**Total**
	Port 1	***Port 2***	***Port 3***	
Naphthalene	0.0075	0.0066	0.089	0.1031
Acenaphthylene	0.065	0.054	0.039	0.158
Acenaphthene	0.052	0.045	0.068	0.165
Phenanthrene	0.0052	0.0046	0.0060	0.0158
Anthracene	0.099	0.087	0.098	0.284
Fluoranthene	0.0064	0.0077	0.0089	0.023
Fluorene	0.0095	0.0097	0.086	0.1052
Pyrene	0.035	0.045	0.069	0.149

BaA	0.469	0.337	0.298	1.104
Chrysene	2.64	2.22	3.01	7.87
Bbf	0.960	0.890	0.490	2.34
BKF	5.56	6.06	3.99	15.61
Bap	0.192	0.198	0.320	0.71
Indeno Pyrene	0.419	0.559	0.097	1.075
DBA	0.192	0.290	0.245	0.727
Benzo (ghi) perylene	0.0099	0.0130	0.015	0.0379
TOTAL (PAHs)	**10.7215**	**10.8266**	**8.9289**	**30.477**

Tables 4. Aromatic hydrocarbons in the Marine Shell (Patella.) samples in areas (Port 1, Port 2, Port 3).

Compound	***Shell Patella.***			**Total**
	Port 1	***Port 2***	***Port 3***	
Naphthalene	0.122	0.057	0.045	0.157
Acenaphthylene	0.0099	0.050	0.200	0.2
Acenaphthene	0.089	0.076	0.066	0.173
Phenanthrene	0.0050	0.086	0.030	0.0894
Anthracene	0.0098	0.065	0.059	0.101
Fluoranthene	0.0096	0.0068	0.0075	0.0169
Fluorene	0.0054	0.060	0.088	0.1045
Pyrene	0.210	0.300	0.500	0.824
BaA	0.070	0.234	0.0111	0.1724
Chrysene	2.320	4.09	5.01	8.7
Bbf	1.980	1.580	1.90	2.46
BKF	2.10	4.460	3.790	7.18
Bap	0.307	0.180	0.019	0.195
Indeno Pyrene	0.055	0.108	0.266	0.296
DBA	0.233	0.256	0.342	0.557
Benzo (ghi) perylene	0.019	0.021	0.0581	0.054
TOTAL (PAHs)	**4.192**	**8.0819**	**9.0063**	**21.2802**

DISCUSSION

Temperature is one of the most important environmental factors, which directly affects the aquatic ecosystem. The direct effect on the metabolic activities of most aquatic organisms caused by temperature variations is controlled by Van HofPs law according to which the rate of biological processes may increase two or three times with a rise of temperature of 10°C within the tolerable limit [8]. The pH value of open seawater is nearly constant, and only at exceptional

circumstances it falls outside the range of 7.8 - 8.3, such constancy is a result of the buffer capacity of seawater. The bulk of which can be attributed to the dissolved carbon dioxide and the carbonate and bicarbonate ions [10]. Smith pointed out that the decrease in the pH-value is coincided with the decrease in oxygen content [11]. This indicated in the present study by the positive significant correlation between pH and DO (r = 0.358). The main factors controlling the distribution of pH in the marine environment are; dissolved oxygen, water temperature, sewage discharge, decomposition of organic matter, photosynthetic activity of aquatic plants, respiration of aquatic organisms, as well as some physicochemical processes, such as precipitation and oxidation reduction processes taking place in the environment so, it is not surprising to find obvious seasonal, monthly and diurnal variations [12]. Hydrogen ion concentration plays an important role in many life processes, living organisms are very dependent on and sensitive to pH-value.

DO is a fundamental requirement for the aquatic organisms, it affects their biological processes and is needed in the aerobic oxidation of the organic matter in water and sediments [13]. In the latter process, complex organic substances are converted to simple dissolved inorganic salts, which could be utilized by micro and macrophyta and shell.

PAHS which obtained and detected by GC-Mass instrument in this study including (Naphthalene, Acenaphthylene, Acenaphthene, Fluorine, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo (a) anthracene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Dibenzo (a, h) anthracene, Benzo(ghi) Perylene, andindeno, (1,2,3-cd) Pyrene.

In general, the ∑PAHs contents which recorded in this study were lower than that recorded for the Spain coasts (7780 µg/g) [14, 15], also lower than Alexandria coast (Egypt) with 61.87 µg/g [16].

The present study suggests that the values of PAHs were 7.456, 9.454 and 8.967 µg/g. it is to some extent safe and will have weak. but not harmful, effect on marine organisms. This is in accordance with reported. Previous study concluded that the total hydrocarbons concentration in marine which can produce a harmful effect on the aquatic organisms with about 50 µg/l [17].

The present investigation briefly concludes that the sources of PAHs in the studied area are mainly from incomplete combustion at high temperatures of recent and fossil organic matter (Pyrolyric origin) with little evidence of petro genic origins. Atmospheric deposition, industrial discharges and land runoff waters are the main Factors responsible for pyrolytic PAHs [18].

CONCLUSION

This study has satisfied the aims and objectives by analyzing the hydrocarbons concentrations of marine in shell taken from area Al Jabal Al - Akhdar- for port in Darnh city. The detailed study of the distribution and origin of petroleum hydrocarbons in three locations collected from Al Jabal Al - Akhdar- for port in Darnh City. The results showed that most f the studied samples containing aromatic hydrocarbons.

Conflict of Interest

There are no financial, personal, or professional conflicts of interest to declare. Conflict of Interest

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الكشف عن المركبات العطرية في بعض عينات Shell بساحل درنة

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المستخلص
الخلفية والأهداف. الهيدروكربونات العطرية متعددة الحلقات (PAH) هي فئة واسعة الانتشار من الملوثات الكيميائية البيئية ذات الخصائص المسببة للطفرات والمسرطنات ويمكن أن تتراكم في مصفوفات مختلفة من البيئة المائية. هدفت هذه الدراسة إلى تقييم درجة التلوث بواسطة الهيدروكربونات العطرية متعددة الحلقات للرواسب الساحلية في المناطق غير الصناعية في البحر الأبيض المتوسط. **طُرق الدراسة**. تمتد منطقة الدراسة على طول ساحل مدينة ميناء درنة بحوالي 4 كم شرق مدينة الدرنة. تم اختيار ثلاثة مواقع. تم تحديد الهيدروكربونات في Shell. تم تحليل العينات بحثا عن الهيدروكربونات العطرية باتباع خطوات مختلفة منها: الاستخراج والتنظيف والتجزئة والتحليل الآلي ومراقبة الجودة التحليلية. **النتائج**. أظهرت النتائج أن المحتوى العالي من الهيدروكربونات العطرية متعددة الحلقات تم تسجيله في موقع الميناء (1،2) ، في عينات القشرة البحرية (Monodonta) بقيم (10.72 و 10.82 ميكروغرام / جم) على التوالي ، ومحتويات الهيدروكربونات العطرية متعددة الحلقات في قذائف Monodenta كانت على النحو التالي (8.92 ميكروغرام / جم) لمواقع المنفذ 3. وعلى الجانب الآخر كانت محتويات قشرة PHAs في المنفذ 3. على الجانب الآخر . (g / gو (9.0 ميكروغرام / جم) في مواقع المنفذ 1،2،3 ، على التوالي. **الخاتمة**. استوفيت هذه الدراسة تركيز الهيدروكربونات البحرية في الصدف المأخوذ من منطقة الجبل الأخضر لميناء مدينة درنة ، حيث احتوت معظم العينات المدروسة على الهيدروكربونات العطرية.
الكلمات الدالة. المحروقات ، Shell ، درنة ، الساحل ، عطري.