PROCEEDINGS BOOK
12th ICEEE–2021
"Global Environmental Development & Sustainability: Research, Engineering & Management"
November 18 – 19, 2021 RKK – Óbuda University, Budapest, Hungary
ISBN: 978-963-449-256-6 **www.iceee.hu**

OIL POLLUTION IN THE PORT OF BENGHAZI CITY, NE LIBYA

Osama R. SHALTAMI[1], Fares F. FARES[1], Osama A. El-FALLAH[1*], Farag M. EL OSHEBI[1], Hwedi ERRISHI[2] and Salah S. El-EHFIFI[3]

[1]*Department of Earth Sciences, Faculty of Science, Benghazi University, Libya*
[2]*Department of Geography, Faculty of Arts, Benghazi University, Libya*
[3]*National Oil Corporation (NOC), Exploration Department, Libya*

Abstract: *This work represents the first comprehensive survey of polycyclic aromatic hydrocarbons (PAHs) in beach sands of the Port of Benghazi city northeast Libya. The analysed PAHs are originated mainly from pyrolytic sources. The carcinogenic PAHs such as benzo [a] anthracene (BaA), chrysene (Chr), benzo [b] fluoranthene (BbF), benzo [k] fluoranthene (BkF), benzo [a] pyrene (BaP), Dibenzo [a,h] anthracene (DahA) and indeno [1,2,3-cd] perlyene (IP) are observed in all samples. The risk evaluation revealed the exceedingly high environmental risk of PAHs in the beach sands.*

Keywords: *Aromatic Hydrocarbons, environment, Libya, Oil Pollution, Polycyclic, Port of Benghazi.*

INTRODUCTION

Benghazi city is located in northeast of Libya; it is the second largest city in Libya. The Port of Benghazi (32° 6′ 33″ N 20° 2′ 51″ E, Figure 1) is a major seaport in the city. There are three main sources of pollution in the port, namely oil (ship fuel), sewage disposal and paints. The aim of this work is to assess the oil pollution in the Port of Benghazi. To achieve this goal, we evaluated thelevels of polycyclic aromatic hydrocarbons (PAHs) in the beach sands of the port. The port is clearly contaminated with oil (Figure 2).

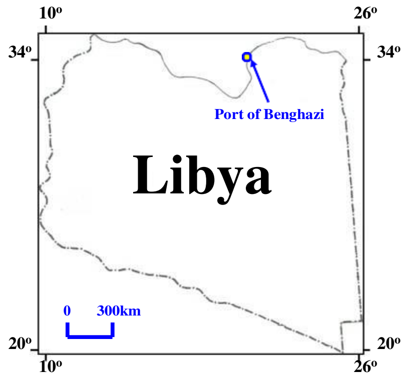

Figure 1.: Location map of the Port of Benghazi.

Figure 2.: Oil pollution in the Port of Benghazi.

On the basis of published papers, we believe that this study is the first evaluation of PAHs in the Port of Benghazi. There are some studies on PAHs in other areas of Libya (e.g., Bonsignore et al., 2018; Alsarawi, 2021). However, most of the pollution studies on the Libyan coast have focused on heavy metals (e.g., Hamouda and Wilson, 1989; Shaltami, 2012, 2014, et al., 2019).

METHODOLOGY

Three samples were collected from the studied sands. We took the samples from a depth of 30 cm. The samples were stored at -20°C until analysis. Identification of PAHs were done using HPLC (Perkin Elmer series 200) with photodiode array detector. The analysis was carried out in the StratoChem in Egypt.

RESULTS AND DISCUSSION

1. Levels of PAHs

Table 1 shows the concentrations of PAHs in the studied sands. The carcinogenic PAHs (BaA, Chr, BbF, BkF, BaP, DahA, and IP) are detected in all samples. There is a large difference in the concentrations of individual PAHs (e.g., Flu ranges from 635.61 to 5892.82 ng/g) and total PAHs (44073.19-*75580.65* ng/g). However, the highest concentration of total PAHs is recorded in sample b2. There are four groups of relative pollution level, namely low (0-100 ng/g), moderate (100-1000 ng/g); high (1000-5000 ng/g); and very high (>5000 ng/g) (Baumard et al., 1998). Obviously, the pollution level in the studied sands is very high. The composition patterns of PAHs by ring size in the studied sands are presented in Figure 3.

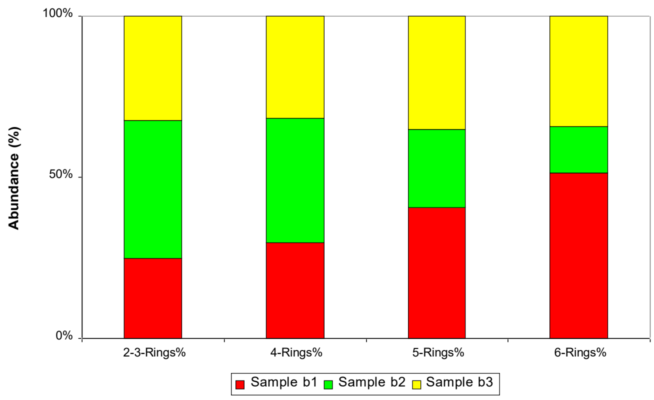

Figure 3.: Distribution of PAHs in the beach sands of the Port of Benghazi according to the number of aromatic rings

Table 1. Concentration of PAHs (ng/g) in the beach sands of the Port of Benghazi

Parameters	Sample No.		
	b1	b2	b3
Nap	2520.40	16103.33	2109.52
A	521.55	1301.42	7971.91
Ace	5743.55	4631.52	7441.50
Phe	722.19	1193.14	202.93
F	462.00	639.54	739.64
Ant	922.91	8291.64	784.48
Total 2- to 3-Ring	10892.60	32160.59	19249.98
Flu	635.61	5892.82	1870.45
Pyr	701.76	8482.76	2500.34
BaA	1834.87	1775.30	1993.77
Chr	6220.20	4720.98	7304.64
Total 4-Ring	9392.44	20871.86	13669.20
BbF	804.70	359.50	910.08
BkF	18443.51	19402.67	22011.71
BaP	589.67	483.54	660.92
DahA	1011.43	899.97	1009.74
Total 5-Ring	20849.31	21145.68	24592.45
BP	2253.17	1073.78	2413.90
IP	685.67	328.74	255.94
Total 6-Ring	2938.84	1402.52	2669.84
Total PAHs	44073.19	75580.65	60181.47

Source of PAHs

There are two sources of PAHs in marine sediments, namely pyrogenic and petrogenic. In general, petrogenic substances include crude oil and refined crude oil products such as gasoline, heating oil, asphalt, and coal. Pyrogenic substances are complex mixtures of primarily hydrocarbons produced from organic matter subjected to high temperatures but with insufficient oxygen for complete combustion.

Pyrogenic PAHs are produced by fires, internal combustion engines, and furnaces. They also are formed when coke or gas are produced from coal or oil. Coal-tar based products, such as roofing, pavement sealers, waterproofing, pesticides, and some shampoos contain pyrogenic PAHs (Lingle, 2008).

Pyrolytic PAHs are characterized by compounds with four or more aromatic rings, whereas petrogenic PAHs contain only two or three aromatic rings (Wang et al., 2010).

The ratios of low molecular weight PAHs (LMW) to high molecular weight PAHs (HMW), Phe/Ant, Flu/(Flu+Pyr) and BaA/(BaA+Chr) were used to identify the source of PAHs in the studied sands. Sediments with low values of LMW/HMW and Phe/Ant (<1 and <10, respectively) indicate pyrolytic sources, whereas high values of LMW/HMW and Phe/Ant (>1 and >10, respectively) is typical of petrogenic source (Ahmed et al., 2017).

In this study, the LMW/HMW and Phe/Ant ratios (Table 2) suggest that pyrogenic sources are the main origin of the analyzed PAHs (Figures. 4 and 5). Moreover, the binary diagrams (Figures. 6 and 7) indicate the dominant of liquid fossil fuel combustion.

Table 2. Isomeric ratio of PAHs in the beach sands of the Port of Benghazi

Parameters	Sample No.		
	b1	b2	b3
LMW	10892.60	32160.59	19249.98
HMW	33180.59	43420.06	40931.49
LMW/HMW	0.33	0.74	0.47
Phe/Ant	0.78	0.14	0.26
Flu/(Flu+Pyr)	0.48	0.41	0.43
BaA/(BaA+Chr)	0.228	0.273	0.2144

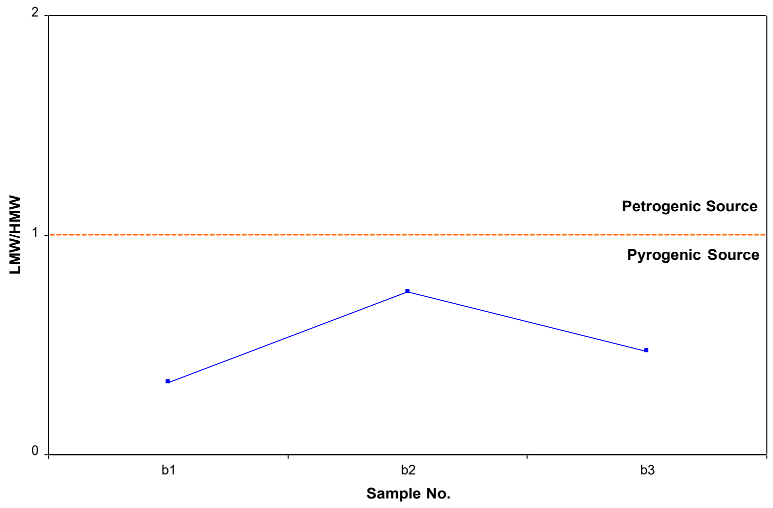

Figure 4.: Binary diagram showing the source of PAHs in the beach sands of the Port of Benghazi (fields after Ahmed et al., 2017).

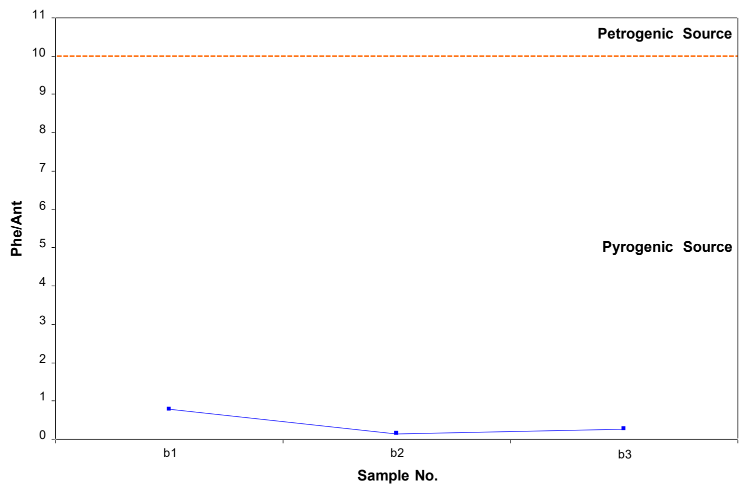

Figure 5.: Binary diagram showing the source of PAHs in the beach sands of the Port of Benghazi (fields after Ahmed et al., 2017).

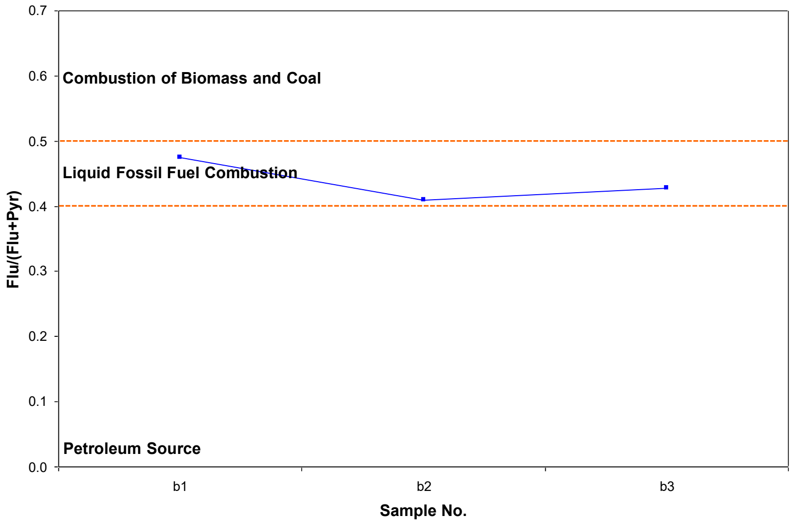

Figure 6.: Binary diagram showing the source of PAHs in the beach sands of the Port of Benghazi (fields after Yunker et al., 2002).

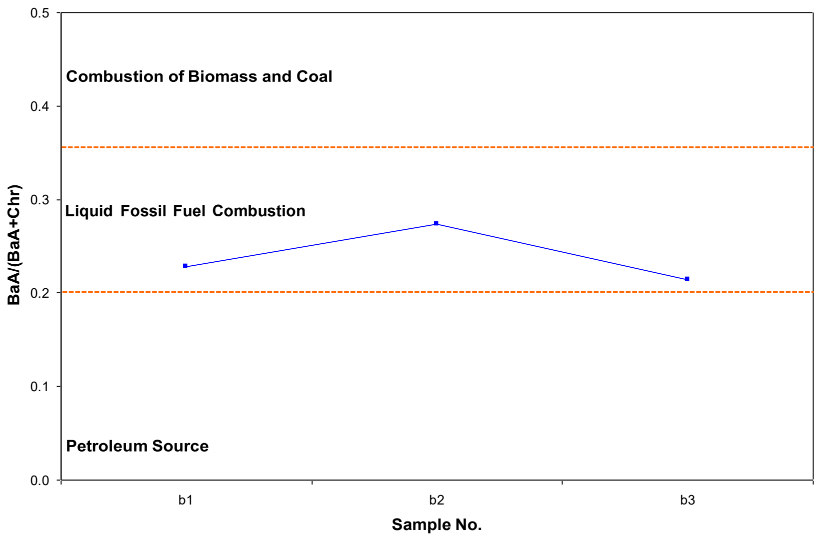

Figure 7.: Binary diagram showing the source of PAHs in the beach sands of the Port of Benghazi (fields after Yunker et al., 2002).

Where: Nap = Naphthalene, A = Acenaphthylene, Ace = Acenaphthene, Phe = Phenanthrene, F = Fluorine, Ant = Anthracene, Flu = Fluoranthene, Pyr = Pyrene, BaA = Benzo [a] anthracene, Chr = Chrysene, BbF = Benzo [b] fluoranthene, BkF = Benzo [k] fluoranthene, BaP = Benzo [a] pyrene, DahA = Dibenzo [a,h] anthracene, BP = Benzo [g,h,i] perlyene, IP = Indeno [1,2,3-cd] perlyene

Sediment Quality Guidelines (SQGs)

Sediment Quality Guidelines (SQGs) provide two target values: effects range low (ERL) and effects range median (ERM), which are established using the 10th and 50th percentiles, respectively, in a database of increasing concentrations associated with adverse biological effects. PAH concentrations lower than ERL are considered not to be harmful to organisms, while concentrations higher than ERM are considered to be harmful frequently. PAHs with concentrations between ERL and ERM are considered to be harmful occasionally (MacDonald et al., 2000). The SQGs are shown in Table 3. Clearly, the ERM is below the concentrations of Nap, A, Ace, BaA, Chr, BkF, DahA and Bp, while the concentrations of F, Phe, Ant, Flu, Pyr, BbF, and BaP are between the ERL and ERM (Figure 8).

Table 3. Sediment Quality Guidelines (after MacDonald et al., 2000)

	Guideline SQG	
	ERL	ERM
Nap	160	2100
A	16	500
Ace	44	640
F	19	540
Phe	240	1500
Ant	85.3	1100
Flu	600	5100
Pyr	665	2600
BaA	261	1600
Chr	384	2800
BbF	320	1880
BkF	280	1620
BaP	430	1600
DahA	63.4	260
BP	430	1600

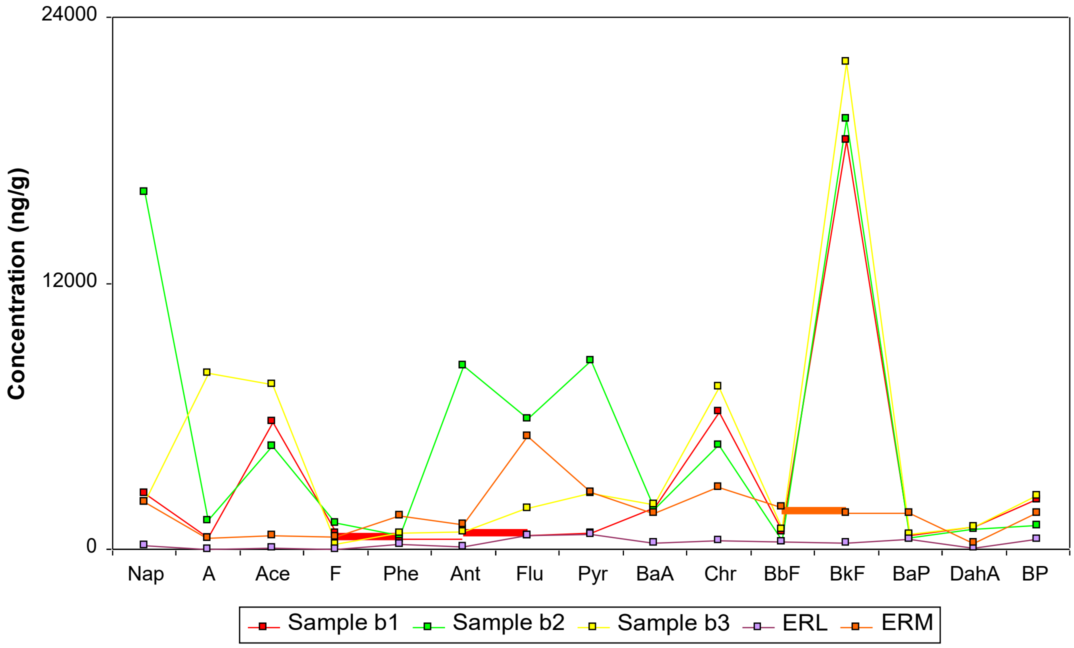

Figure 8.: Comparison of ERL and ERM with PAH concentrations in the beach sands of the Port of Benghazi.

Moreover, the levels of PAHs are compared against their corresponding quality values to evaluate potential ecosystem risk of PAHs in the studied sands. Table 4 shows the reference values that were used in this study. We applied equations (1) and (2) to determine the values of RQNCs and RQMPCs:

$$RQNCs = CPHAS/CQV(NCs) \quad (1)$$

$$RQMPCs = CPHAS/CQV(MPCs) \quad (2)$$

Table 4. NCs and MPCs of PAHs in sediments (concentrations in ng/g, after Cao et al., 2010)

Parameters	NCs	MPCs
Nap	1.4	140
A	1.2	120
Ace	1.2	120
Phe	5.1	510
F	1.2	120
Ant	1.2	120
Flu	26	2600
Pyr	1.2	120
BaA	3.6	360
Chr	107	10700
BbF	3.6	360
BkF	24	2400
BaP	27	2700
DahA	27	2700
BP	75	7500
Total PAHs	364.7	36470

Where CPAHs is the concentration of certain PAHs in the studied sands, CQV(NCs) and CQV(MPCs) are the quality values of the NCs and MPCs of PAHs in sediments, respectively. However, the risk classification of individual PAHs and total PAHs is presented in Table 5. Generally, the values of RQMPCs of the individual PAHs (except for Flu, Chr, BaP, DahA and BP) and total PAHs are higher than 1 (Table 6), which indicates that the biota in the beach sands of the Port of Benghazi is at high risk and suffered from severe toxicity.

Table 5. Risk classification of individual PAHs and ΣPAHs (after Cao et al., 2010)

Class	Individual PAHs		Class	ΣPAHs	
	RQ_{NCs}	RQ_{MPCs}		$RQ_{\Sigma PAHs(NCs)}$	$RQ_{\Sigma PAHs(MPCs)}$
Risk-free	0		Risk-free	0	
			Low-risk	≥1;<8	0
Moderate-risk	≥1	<1	Moderate-risk$_1$	≥800	0
			Moderate-risk$_2$	<800	≥1
High-risk		≥1	High-risk	≥800	≥1

Table 6. RQNCs and RQMPCs values in the beach sands of the Port of Benghazi

Parameters	Sample No.					
	b1		b2		b3	
	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}
Nap	1800.29	18.00	11502.38	115.00	1506.80	15.07
A	434.63	4.35	1084.52	10.85	6643.26	66.43
Ace	4786.29	47.86	3859.60	38.60	6201.25	62.00
Phe	141.61	1.42	233.95	2.34	39.79	0.40
F	385.00	3.85	532.95	5.33	616.37	6.16
Ant	769.09	7.69	6909.70	69.10	653.73	6.54
Flu	24.45	0.24	226.65	2.27	71.94	0.72
Pyr	584.80	5.85	7068.97	70.69	2083.62	20.84
BaA	509.69	5.10	493.14	4.93	553.83	5.54
Chr	58.13	0.58	44.12	0.44	68.27	0.68
BbF	223.53	2.24	99.86	1.00	252.80	2.53
BkF	768.48	7.68	808.44	8.08	917.15	9.17
BaP	21.84	0.22	17.91	0.18	24.48	0.24
DahA	37.46	0.37	33.33	0.33	37.40	0.37
BP	30.04	0.30	14.32	0.14	32.19	0.32
Total PAHs	120.85	1.21	207.24	2.07	165.00	1.65

CONCLUSIONS

The main conclusions are as follows:
1) The PAHs pollution in the beach sands of the Port of Benghazi is mainly caused by pyrogenic sources.
2) The carcinogenic PAHs (BaA, Chr, BbF, BkF, BaP, DahA, and IP) are detected in all samples.
3) The biota in the beach sands is at extremely high environmental risk.

RECOMMENDATION

There are several techniques for the degradation of PAHs in sands such as biostimulation techniques.

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