EVALUATION OF PRODUCED WATER IN THE EL FEEL OIL FIELD, MURZUQ BASIN, SW LIBYA

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ABSTRACT:

The aim of this study was to investigate the contamination of polycyclic aromatic hydrocarbons (PAHs) in produced water in well F1-NC174 in the El Feel oil field, Murzuq Basin, SW Libya. The results showed that the produced water contains high contents of TDS, Na and Cl (hypersaline water, NaCl type). Most values of individual PAHs in the produced water are higher than that of the Annual Average Environmental Quality Standards (AA-EQS) of European Water Framework Directive (WFD) for individual PAHs. The carcinogenic PAHs (benzo [a] anthracene, chrysene, benzo [b] fluoranthene, benzo [k] fluoranthene, benzo [a] pyrene, Dibenzo [a,h] anthracene and indeno [1,2,3-cd] perlyene) are observed in all samples.

تقييم المياه المنتجة في حقل الفيل النفطي بحوض مرزق جنوب غرب ليبيا

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ملخص

الهدف من هذه الدراسة هو دراسة تلوث الهيدروكربونات العطرية متعددة الحلقات (PAHs) في المياه المنتجة في البئر F1-NC174 في حقل الفيل النفطي، حوض مرزق، جنوب غرب ليبيا. أظهرت النتائج أن المياه المنتجة تحتوي على نسبة عالية من المواد الصلبة الذائبة والصوديوم والكلور (المياه شديدة الملوحة من نوع NaCl).معظم قيم الهيدروكربونات العطرية متعددة الحلقات في المياه المنتجة أعلى من متوسط معايير الجودة البيئية السنوية (AA-EQS) للتوجيه الإطاري للمياه الأوروبي (WFD) للهيدروكربونات العطرية متعددة الحلقات الفردية. الهيدروكربونات العطرية متعددة الحلقات المسببة للسرطان (بنزو [أ] أنثراسين، كريسين، بنزو [ب] فلورانثين، بنزو [ك] فلورانثين، بنزو [أ] بيرين، ديبنزو [أ، ح] أنثراسين وإنديدنو [1،2،3-سي دي] بيرلين) شهدت في جميع العينات.

الكلمات الدالة : المياه المنتجة، الهيدروكربونات العطرية متعددة الحلقات، حقل الفيل النفطي، حوض مرزق، ليبيا.

INTRODUCTION

The El Feel (Elephant) oil field is the most recent to be discovered and the smallest of Libya's 21 big fields in terms of reserves.It is located 70 km southwest of the A-NC 115 oil field and 45 km south of the B-NC 115 oil field in the northern Murzuq Basin (Fig.1) (Hallett and Clark-Lowes, 2016). In contrast to the fields of the El Shararah trend, the structure is an extended, fault-bounded, three-way dip closure (Fig. 2). Produced water is a complex mixture of particulate organic, dissolved, and inorganic chemicals. The geologic age, depth, and geochemistry of the hydrocarbonbearing deposit, the chemical makeup of the oil and gas phases in the reservoir, and the production chemicals added to the production AMEC (2006) all have a significant impact on the physical and chemical characteristics of the produced water. Several naturally occurring substances that were dissolved or dispersed by the geologic formations and pathways of migration that the generated water resided for millions of years can be found in produced water. These substances include metals, radioisotopes, inorganic salts, and a broad range of organic compounds, mostly hydrocarbons. (Shaltami, 2022).

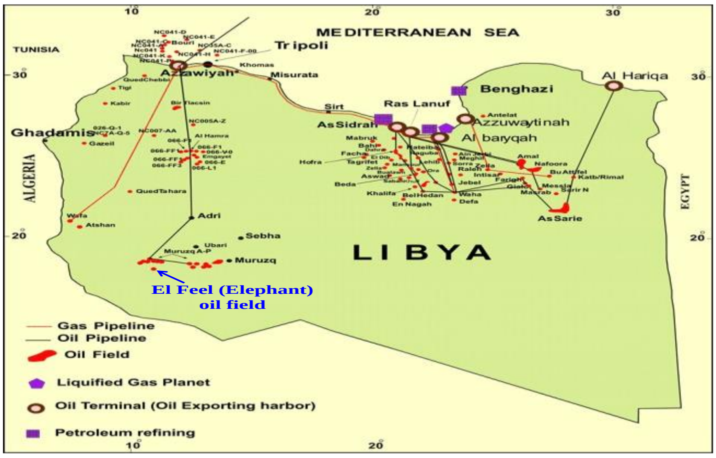

Fig. (1): Location map of the El Feel oil field (after Shaltami *et al*., 2020).

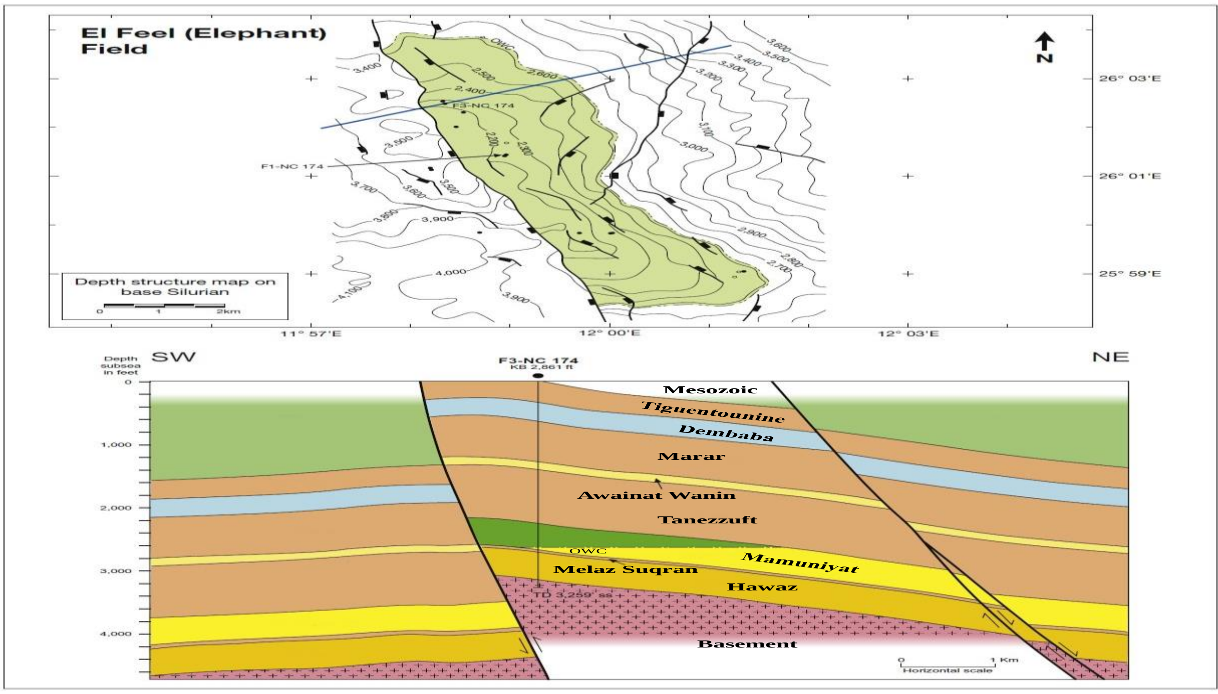

Fig. (2): Depth structure map on the base Silurian with south-west to north-eastcross-section. Contour interval 100 ft.

Separate identification is provided for the discovery well F1-NC 174. The vertical exaggeration is ×5, and the cross-section is through the major reservoir interval. According to Hallett and Clark-Lowes (2016), OWC stands for original oil-water contact.

1.1.Present Study

This work is an environmental study of oilfield waters produced from the Mamuniyat Reservoir (sandstone) in well F3-NC 174 in the El Feel oil field, Murzuq Basin, SW Libya (Figs. 1 and 2).

1.1.1.Objectives

The main goals of the current study are as follows:

1. Chemical analysis of ions to determine salinity of the produced water.
2. Chemical analysis of polycyclic aromatic hydrocarbons (PAHs) with focusing on the potentially toxic and environment sensitive hydrocarbons.
3. Proposing the adequate solutions.

1.2. Previous Work

Shaltami *et al.,* (2020) conducted a hydrochemical study of produced water in well F1-NC174 in the El Feel oil field. They found the following:

1. The produced waters are brines.
2. The produced waters are of NaCl type.
3. The produced waters have a complex origin and evolution.
4. The gas/oil ratio (GOR) indicates light oil invasion.

We believe that this work is the first assessment of PAHs in the generated water in well F3-NC 174, based on the publications.

METHODOLOGY

Sampling

A total of four produced waters were sampled from well F3-NC174.Potential of hydrogen (pH) and total dissolved solids (TDS) were defined by Denver Instrument Model 50 . Major ions (potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), chloride (Cl), sulfate (SO_4) and bicarbonate (HCO_3) were determined by inductively coupled plasma-mass spectrometry. These analyses were carried out in the National Water Research Center, Ministry of Water Resources and Irrigation of Egypt. Moreover, PAHs (naphthalene (Nap), acenaphthylene (A), acenaphthene (Ace), phenanthrene (Phe), fluorene (F), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo [a] anthracene (BaA), chrysene (Chr), benzo [b] fluoranthene (BbF), benzo [k] fluoranthene (BkF), benzo [a] pyrene (BaP), dibenzo [a,h] anthracene (DahA), benzo [g,h,i] perylene (BP), and indeno [1,2,3-cd] perlyene (IP)) identification and quantification in the extracted oil were performed using HPLC (Perkin Elmer series 200) with photodiode array detector . This analysis was done in the StratoChem in Egypt.

2.1.Water Classification

Water can be classified by the level of total dissolved solids (TDS) in the water:

1. Fresh water (TDS is less than 1,000 ppm).
2. Brackish water (TDS range from 1,000 to 10,000 ppm).
3. Saline water (TDS range from 10,000 to 35,000 ppm).
4. Hypersaline water (TDS greater than 35,000 ppm, (Fetter,C.W.1994; Shaltami, 2022).

In the present study, the TDS values (Table 1 and Fig.3) indicate that the produced water in well F3-NC 174 is of hypersaline type.

Table 1: The data analysis (concentrations in mg/l) of the produced water in well F3-NC 174

Parameters	Sample No.			
	F1	F2	F3	F4
pH	8.24	8.16	8.35	8.32
TDS	35152.00	46727.00	40412.00	38257.00
K	200.68	215.18	247.97	259.00
Ca	539.48	699.98	784.00	555.15
Na	5010.22	6115.09	3809.00	2823.65
Mg	105.17	128.36	115.68	87.52
Cl	9899.76	10989.70	11647.60	10844.00
HCO_3	765.90	549.54	500.31	645.45
SO_4	218.98	384.55	277.71	404.93

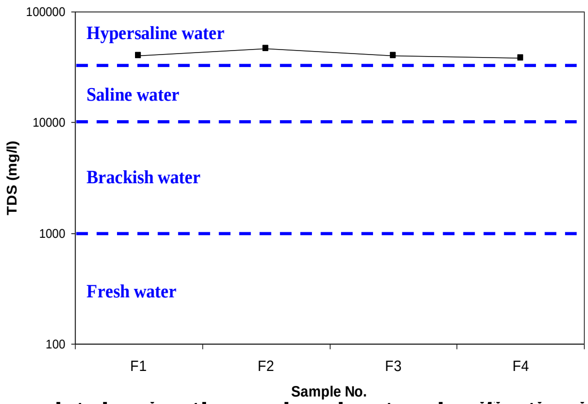

Fig. (3) : Binary plot showing the produced water classification in well F3-NC 174.

2.1.1. Piper Diagram

In hydrochemical investigation, the Piper diagram (1953) provides an efficient graphic representation of the chemistry in water samples. This process depends on the concept that the proportions of cations and anions in water are such that the dissolved salts are electroneutral, or that the algebraic sum of the cations' and anions' electric charges is zero.

Separate triple plots are used to display the cations and anions. Calcium, magnesium, and sodium plus potassium cations are the apexes of the cation plot. Sulfate, chloride, carbonate, and hydrogen carbonate anions are the apexes of the anion plot. Thereafter a diamond is projected with the two ternary plots. A graph of the anions (sulfate + chloride/total anions) and cations (sodium + potassium/total cations) is transformed into a matrix to create the diamond. The Piper diagram can be used to compare the ionic composition of a collection of water samples.

The Piper diagram's water samples can be categorized into hydrochemical facies. According to the dominant cation or anion, the cation and anion triangles can be divided into areas, and their combination forms regions in the diamond-shaped portion of the diagram (Shaltami, 2022).The hydrofacies of the produced water in well F3-NC 174 was determined using the Piper diagram (Fig. 4). Clearly, the water samples are of NaCl type.

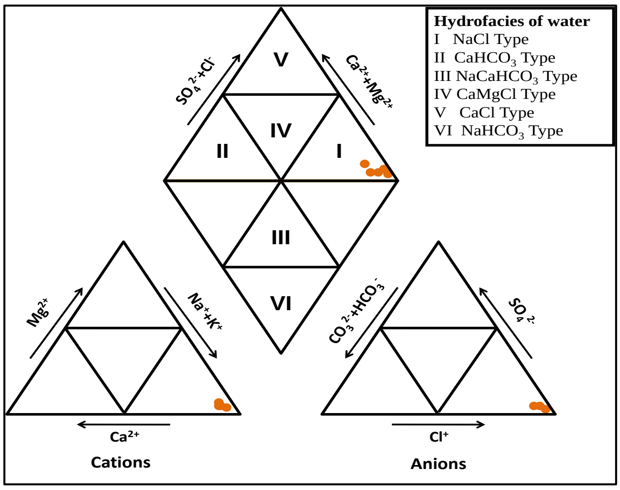

Fig. 4: Piper diagram showing the hydrochemical facies of the produced water classification in well F3-NC 174 (fields after Tweed *et al.*, 2005).

2.2. Levels of PAHs

Polycyclic aromatic hydrocarbons (PAHs) are a common class of compounds found in the environment that include two or more aromatic rings. due to their toxicity, mutagenicity, persistence, and carcinogenicity (Huang et al., 2012; Ahmed et al., 2017). PAHs are of particular concern, and 16 priority PAHs are regulated by the United States Environmental Protection Agency (USEPA).

Although anthropogenic activity is often regarded as the primary source of PAHs, they can also come from natural sources (Baumard et al., 1998). The two main sources of anthropogenic PAHs in the environment are petrogenic and pyrogenic sources. The levels of PAHs in the generated water from well F3-NC 174 were displayed in (Table 2 and Fig. 5). Descriptive statistics were used to make sense of the available data (Table 3 and Fig.6).

Table 2: Concentration of PAHs (ng/L) in the produced water in well F3-NC 174

Parameters	Sample No.			
	F1	F2	F3	F4
Nap	54719.27	22109.00	19447.53	11988.50
A	2964.46	1314.97	5511.84	3000.34
Ace	383760.22	4878.65	40531.72	6019.42
Phe	253.31	986.43	303.90	567.00
F	112.23	315.33	777.64	198.51
Ant	1354.64	7986.86	6638.22	5756.11
Total 2- to 3-Ring	443164.13	37591.24	73210.85	27529.88
Flu	1000.61	8444.67	494.91	661.76
Pyr	566.00	461.56	600.92	283.10
BaA	60.11	32.31	21.07	15.56
Chr	600111.84	498812.18	1119282.31	232470.76
Total 4-Ring	601738.56	507750.72	1120399.21	233431.18
BbF	36.00	57.17	60.61	82.71
BkF	49962.27	18340.91	18773.44	19431.43
BaP	331.61	288.00	559.28	313.72
DahA	1019.75	1313.78	991.57	809.43
Total 5-Ring	51349.63	19999.86	20384.90	20637.29
BP	557.09	779.62	434.00	610.64
IP	196.00	187.44	217.98	279.63
Total 6-Ring	753.09	967.06	651.98	890.27
Total PAHs	1097005.41	566308.88	1214646.94	282488.62

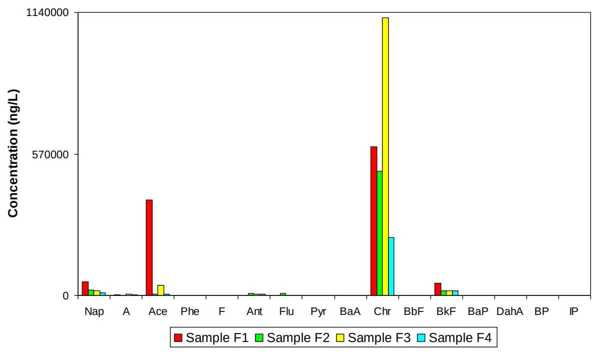

Fig. (5): Concentration of PAHs in the produced water in well F3-NC 174.

Table 3: Descriptive statistics of PAHs (ng/L) in the produced water in well F3-NC 174

Parameters	N	Minimum	Maximum	Mean	Std. Deviation
Nap	4	11988.50	54719.27	27066.08	18926.59
A	4	1314.97	5511.84	3197.90	1731.40
Ace	4	4878.65	383760.22	108797.50	184053.59
Phe	4	253.31	986.43	527.66	335.34
F	4	112.23	777.64	350.93	296.40
Ant	4	1354.64	7986.86	5433.96	2870.09
Flu	4	494.91	8444.67	2650.49	3868.51
Pyr	4	283.10	600.92	477.90	142.72
BaA	4	15.56	60.11	32.26	19.83
Chr	4	232470.76	1119282.31	612669.27	371631.00
BbF	4	36.00	82.71	59.12	19.12
BkF	4	18340.91	49962.27	26627.01	15563.30
BaP	4	288.00	559.28	373.15	125.37
DahA	4	809.43	1313.78	1033.63	208.74
BP	4	434.00	779.62	595.34	143.40
IP	4	187.44	279.63	220.26	41.62

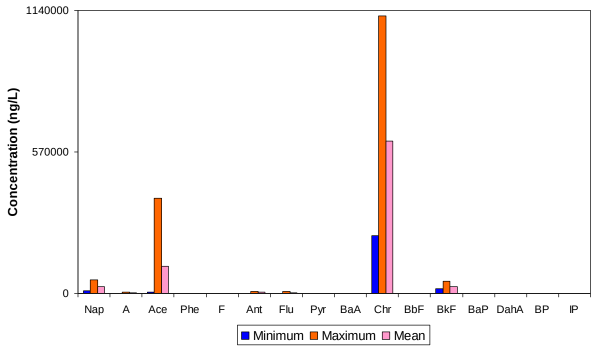

Fig. (6): Descriptive statistics of PAHs in the produced water in well F3-NC 174.

The studied samples contain high concentration of total PAHs (282488.62-1214646.94 ng/L). Various PAH chemicals are found in the water samples at values higher than 10,000 ng/L, indicating that the generated water in well F3-NC 174 is significantly contaminated by PAHs. Nonetheless, (Table 4 and Fig. 7) indicate the PAH content trend for the water samples by ring size.

Table 4: Distribution of PAHs in the produced water in well F3-NC 174 according to the number of aromatic rings

Parameters	Sample No.			
	F1	F2	F3	F4
2-3-Rings%	40.40	6.64	6.03	9.75
4-Rings%	54.85	89.66	92.24	82.63
5-Rings%	4.68	3.53	1.68	7.31
6-Rings%	0.07	0.17	0.05	0.32

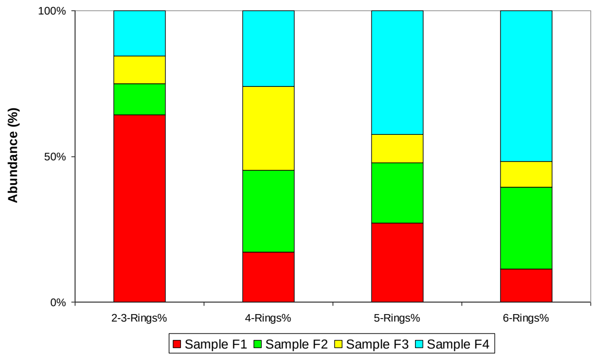

Fig. (7): Distribution of PAHs in the produced water in well F3-NC 174 according to the number of aromatic rings.

Most values of individual PAHs in the produced water in well F3-NC 174 are higher than that of the Annual Average Environmental Quality Standards (AA-EQS) of European Water Framework Directive (WFD) for individual PAHs, which state that the safe range for PAHs is from 20 to 2400 ng/L (Wang *et al.*, 2010). Moreover, the concentration of seven carcinogenic PAHs (BaA, Chr, BbF, BkF, BaP, DahA, and IP) in the water samples are higher than the safe limits of the EPA National Recommended Water Quality Criteria for the protection of aquatic life and human health 20 ng/L (Berry JA, 2004; Omayma *et al.*, 2016). In addition, the most carcinogenic PAHs (i.e. BaA) is detected in all samples, with concentration ranging from 15.56 to 60.11 ng/L; these levels are higher than those of the EPA National

Recommended Water Quality Criteria for the protection of aquatic life 10 ng/L (Omayma *et al.,* 2016).

CONCLUSIONS

This work represents the first comprehensive survey of PAHs in produced water in well F1-NC174 in the El Feel oil field, Murzuq Basin, SW Libya. The main conclusions are as follows:

1. The hydrofacies of the produced water is NaCl type (hypersaline water).
2. The carcinogenic PAHs (BaA, Chr, BbF, BkF, BaP, DahA, and IP) are detected in all samples.
3. Generally, the produced water are heavily contaminated by PAHs.

RECOMMENDATION

Several physical, chemical and biological techniques have been reported to treat water contaminated by PAHs, but adsorption and combined treatment methods have shown better removal performance, with some methods removing up to 99.99% of PAHs.

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