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DETERMINING THE SOURCES AND DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE SOIL OF DIFFERENT OIL FIELDS AT BASRAH GOVERNORATE, IRAQ

The object of the research is polycyclic aromatic hydrocarbons (PAHs). For the purpose of determining the source and distribution of PAHs, soil samples from the 11 oil fields in the Basrah governorate (Seba, Safwan, Majnoon, Ratawi, Bergezia, Qurna1, Qurna2, Shuaaba, South and North Rumaila, and al Zubair) were taken at a depth of 0 to 20 cm. According to their molecular weight, they were separated into two main groupings. The first group of compounds consisted of six compounds: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene. These light (low molecular weight) compounds have two to three fused aromatic rings. The first group includes nine chemicals: fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b), benzo(k), benzo(a), benzo(a), indeno(1,2,3,c,d), and benzo(g,h,i)perylene. These heavy (high molecular weight) compounds included four or more fused aromatic rings. The PAHs compounds ranged in value from the lowest (0.16 ng/g dry weight of benzo(a)anthracene at station West Quarna1) to the highest (680 ng/g dry weight of benzo(g,h,i)perylene that emerged at station North Rumail). The total concentration of PAHs ranged from 77.67 ng/g in South Rumaila Field while highest concentration is 2284.27 ng/g in North Rumail. The PAHs compound has low and high molecular weight, their ratio of LMW/HMW (low molecular weight/high molecular weight) and phenanthrene/anthracene, fluoranthene/pyrene indicated that the source of PAHs was pyrogenic only. The PAH diagnostic ratios and principal component analysis (PCA) indicated that PAHs in soils essentially originated from emissions and combustion. This study gave a baseline on the source and distribution of these compounds in oil fields at Basrah governorate and can be used as a baseline for coming study in the future.

Keywords: polycyclic aromatic hydrocarbons, PAHs, soil pollution, oil fields, Basrah governorate.

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1. Introduction

The soil in Basrah province is suffers from severe pollution with oil pollutants, especially hydrocarbon compounds, normal alkanes (n-alkanes) and polycyclic aromatic hydrocarbons (PAHs) in oil sites and neighboring lands as a result of having many oil fields, increase in drilling operation, exploration to extract oil and due to its refining operations, the accompanying emissions of pollutants and oil spills, and in addition to soil direct pollution, its receives pollutants from the water through leaching and from Air through precipitation and considering that water and air are essential components of the soil.

In addition to the oil fields, Basrah exposed annually to tons of residues resulting from the combustion of gasoline in vehicles, especially since the gasoline and diesel produced in Iraqi refineries do not comply with international environmental specifications, as these two fuels are dangerous pollutants for the Iraqi environment in general.

The other sources of hydrocarbon pollution in Basrah province are power stations that put out large quantities of hydrocarbons and various factories, as well as fuel stations and private electrical generators. All this caused severe pollution with hydrocarbons, which have harmful impacts on the people and environment in Basrah City.

The main ways that people are exposed to PAHs are by eating, skin contact, and inhalation of small particles. Seven chemicals are known to cause cancer, including benzo(a)anthracene, chrysene, benzo(b), benzo(k), benzo(a), pyrene, dibenzo(a), and indeno(1,2,3-c,d). Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, and benzo(g,h,i)perylene are among the nine remaining chemicals that are not carcinogenic.

Total Petroleum Hydrocarbons (TPH) can be divided into four categories based on its structural makeup: aliphatic, aromatic, resinous, and asphaltene. Aromatic hydrocarbons are divided into two classes based on their molecular

structure. Compounds of high molecular weight (HMW) and low molecular weight (LMW) make up these groupings. Traditional wet chemistry approaches rely on «extracting contaminants from a soil sample» in order to calculate the level of TPH. The amount of TPH in the extracted solution is measured using a variety of techniques, including gravimetry calibrated with an Environmental Protection Agency (EPA) calibration standard and gas chromatography-mass spectrometry (GC-MS).

In the fields of the Basra Governorate, eleven samples were taken. These fields stood out due to their expansive geographic area, numerous extractive operations, proximity to the governorate, presence of sizable human settlements inside of them, and presence of river tributaries that serve as a source of water for the areas surrounding those fields. As a result, research should be done to determine how prevalent these pollutants are in particular fields. In order to lessen the effects of oil pollution on the ecosystem in the Basra Governorate, it is crucial since it will serve as a reference for further research. *This study focuses* on the distribution and source of polycyclic aromatic hydrocarbon in these 11 oil fields in the Basrah governorate because it is one of the most significant cities in Iraq and has significant oil reserves nearby. It may serve as a baseline for future research on this topic.

2. Materials and Methods

At eleven locations in the oil field at Basrah city (Seba, Safwan, Majnoon, Ratawi, Bergezia, Qurna1, Qurna2, Shuaaba, South and North Rumaila, and al Zubair) as shown in Fig. 1.

Soil samples were taken in the summer of July 2023. Using aluminium foil to twist the samples, they were then taken to the lab for examination. The method was used to extract the hydrocarbons from the soil by using 250 ml of methanol:benzen (1:1) and 50 g of soil, a 24-hour soxhlet extraction was performed. Activated elemental copper was used to eliminate the elemental sulphur from the extracts in order to prevent sulphur interferences from occurring during the gas chromatographic separation. The extracts were subsequently separated by a chromatography column into aliphatic and aromatic hydrocarbons. The column was made by slurry packing 10 g of silica (100–200 mesh), 10 g of alumina (100–200 mesh) (silica-gel and alumina were activated at 200 °C for 4 hours and then partially deactivated with 5 % water), and then 1 g of anhydrous sodium sulphate was added to the surface to prevent disruption of the top layer when pouring the solvent. The aromatic hydrocarbons were subsequently obtained by adding the extract to the column's head, which eluted 25 ml of benzene. The aromatic

fractions were concentrated using a rotary evaporator, then transferred to a vial, where the volume was precisely set to 1 ml using a stream of N₂. Analyses were performed using an ally capillary gas chromatography with flash ionization detector (FID) on an aliquot of a 1 l extract of aromatic hydrocarbons. The temperature of the column (Agilent 19091J-101HP-5 5 %phenyl Methyl silicone with dimensions for PAHs) was held at 80 °C for 2 minutes before increasing at a rate of 8 °C per minute to 280 °C for 12 minutes. Based on the retention time of an actual mixed standard purchased from Supelco, USA, the individual PAHs were identified. The concentrations of PAHs compounds were determined using the standard calibration curve of the appropriate standard compounds. The range of recovery assays for substances containing PAHs is 80 % to 92 %. Based on replicate analysis, the method's standard deviation was under 10 %. The samples were carefully guarded against contamination during the analysis process. Prior to use, all solvents were double-distilled; glassware was then heated in an oven at 250 °C for 24 hours while being rinsed with distilled water. Procedure blanks, which included all the reagents and glassware used in the analysis, were, however, occasionally identified that had exhibited no discernible interference.

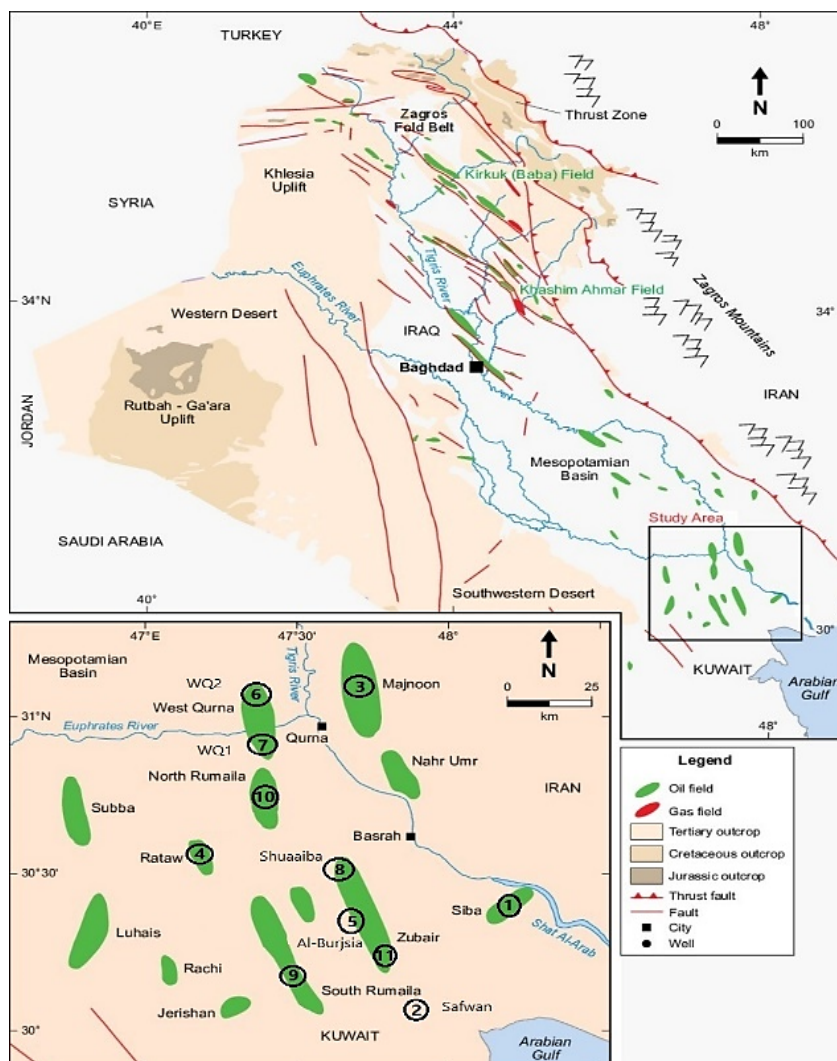


Fig. 1. Samples location

3. Results and Discussion

Fifteen compounds of PAHs were identified in soil samples in the present study in stations 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 – Seba, Safwan, Majnoon, Ratawi, Bergezia, Qurna1, Qurna2, Shuaaba, South and North Rumaila, al Zubair oil field, respectively. According to their molecular weight, they were separated into two main groupings. The first group of compounds consisted of six compounds: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene. These light (low molecular weight) compounds have two to three fused aromatic rings. The second group consisted of nine compounds: benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3,c,d)pyrene, and benzo(g,h,i)perylene. These heavy (high molecular weight) compounds have four or more fused aromatic rings.

The following PAH concentrations were found in soil samples from eleven different locations (Table 1): station 1 from 0.68 ng/g to 53 ng/g, station 2 from 0.86 ng/g to 80 ng/g, station 3 from 0.47 ng/g to 60 ng/g, station 4 from 1.3 ng/g to 30 ng/g, station 5 from 0.9 ng/g to 120 ng/g, station 6 from 0.3 ng/g to 14 ng/g, station 7 from 0.16 ng/g to 120 ng/g, station 8 from 0.7 ng/g to 460 ng/g, station 9 from 0.5 ng/g to 20 ng/g, station 10 from 0.2 ng/g to 680 ng/g and station 11 from 0.5 ng/g to 90 ng/g. The PAH compounds ranged in value from low 0.16 ng/g dry weight of benzo(a)anthracene at station (7) at west Qurna1 oil field to high 680 ng/g of benzo(g,h,i)perylene which occurred at station 10 at North Rumail. The range of the total PAH content was 77.67 at station 9 (South Rumaila Field) and 2284.27 ng/g in station 10 (North Rumail).

Among the light PAHs, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene were the most common compounds. While benzo(a), anthracene, pyrene, fluoranthene, and benzo(k), were the most prevalent heavy PAHs compounds. According to studies by [1, 2] the most potent carcinogens are benzo(a)anthracene and benzo(a)pyrene.

The molecular weight may be the reason why we saw more HMW-PAHs than LMW-PAHs at every station over the course of the investigation. Different groups of microorganisms, such as fungi, algae, and bacteria, were responsible for the different rates at which low and high molecular weight PAHs degraded. Whatever the case, bacteria are crucial to the last stages of mineralization. Higher molecular weight PAHs including pyrene, fluoranthene, benzo(a)anthracene, and benzo(a)pyrene are more resistant to degradation than lower molecular weight PAHs like naphthalene and phenanthrene [3]. In addition, the vapour pressure of PAHs with low molecular weights, like naphthalene, is the highest. As a result, the most significant method of removing these chemicals from the environment is likely their volatilization in the environment [4, 5]. According to the results of the current study's regional PAH analysis, the station (8-Shuaaba) had the greatest concentration of PAHs (680), which was of benzo(g,h,i)perylene, while the station (North Rumail) had the lowest (0.16 ng/g dry weight of benzo(a)anthracene). PAHs can enter the environment from a variety of sources, including: the oil business poses serious risks to the environment and may have an impact on it on various levels, including the air, water, soil, and ultimately all living things in our region. The pollution that results from all activities at all phases of oil and gas production, from exploration activities to refining, is the most pervasive and hazardous effect of the oil and gas industry's activities. Over 800 different chemicals are produced during drilling, production, refining (which is the most polluting process), and transportation wastes, gas emissions, solid waste, and aerosols, with oil and petroleum products predominating among these [6]. The lowest recorded concentration of PAHs in this investigation was 0.16 ng/g dry weight of benzo(a)anthracene at station 7 – WQ1, and the highest recorded concentration of PAHs was 680 ng/g of benzo(g,h,i)perylene, which appeared at station 10 – North Rumail.

Concentrations of PAH compounds (ng/g) dry weight in soil of oil field at Basrah

Table 1

PAHs compounds	St (1) Seba	St (2) Safwan	St (3) Majnoon	St (4) Ratawi	St (5) Bergezia	St (6) Qurna1	St (7) Qurna2	St (8) Shuaaba	St (9) South Rumaila	St (10) North Rumaila	St (11) Zubair
naphthalene	ND	ND	1.2	15	ND	ND	40	40	20	60	90
acenaphthylene	20	ND	60	10	18	16	5	16	ND	0.47	1.1
acenaphthnhen	20	ND	ND	ND	ND	ND	10	ND	18	10	20
fluorene	0.68	ND	0.72	10	22	14	10	3.9	22	20	10
phenanthrene	40	10	0.47	15	12	12	110	80	10	100	70
anthracene	50	7.3	10	15	24	13	120	90	10	120	5.1
fluoranthene	10	20	10	12	8	0.3	40	130	22	130	40
pyrene	20	80	15	30	14	0.4	40	130	32	130	60
benzo(a)anthrac	10	ND	10	15	0.9	4.1	0.16	0	0.6	0.2	0.9
chrysene	10	2.7	20	25	80	10	30	360	7	320	60
benzo(b)fluora	0.87	0.86	0.9	23	3.2	4.3	0.69	1.1	1.9	320	20
benzo(k)fluora	1.69	0.86	0.9	1.3	120	3.9	70	460	0.67	350	20
benzo(a)pyrene	2.4	1	20	2.1	100	1.7	0.9	400	0.5	40	3.2
indeno(1,2,3-cd)pyrene	30	20	ND	ND	10	5	1.5	290	17	3.6	0.5
benzo(g,h,i)perylene	53	10	20	ND	10	4	0.33	0.7	10	680	0.89
ΣPAHs (ng·g ⁻¹)	268.64	152.72	169.19	173.4	422.1	88.7	478.58	2001.7	154.67	2284.27	401.69

Notes: St – station; ND – not detectable

The arrangement of the concentration is as follows: North Rumaila > Shuaaba > West Qurna1 > Bergezia > al Zubair > Seba > Ratawi > Majnoon > Safwan > West Qurna2 > South Rumaila.

The main sources of PAHs in the soil of (Seba, Safwan, Majnoon, Ratawi, Bergezia, Qurna1, Qurna2, Shuaaba, South and North Rumaila, and al Zubair) were pyrogenic and petrogenic origin. The phenanthrene/anthracene ratio ranged from 0.047 at station 3 in Majnoon to 1.37 at station 2 in Safwan. The ratio data indicated that petrogenic and pyrogenic processes were the sources of PAHs in soil (Tables 2, 3).

The percentage of PAHs in different oil field is the percentage of PAHs in different oil field is shown in Fig. 2. The highest percentage (35 %) shown at station 10 (North Rumala) while lower percentage (1.191 %) shown at station 9 (South Rumala).

Table 4 shows the results of the current study in comparison to earlier research in other oil fields in Iraq.

It was discovered that they are higher than certain studies and lower than others; this is because of the location from which the samples were taken, the quantity of contaminants present in it, as well as the population density.

Table 2

PAHs pollution indices values and its origin source descriptions in soil samples at the studied locations during the studied periods

Locations	Ant/(Ant+Phen)	Description	BaA/(BaA+Chry)	Description
1	0.556	pyrolytic	0.5	pyrogenic
2	0.422	pyrolytic	ND	–
3	0.955	pyrolytic	0.333	pyrogenic+petrogenic
4	0.5	pyrolytic	0.375	pyrogenic
5	0.667	pyrolytic	0.011	petrogenic
6	0.52	pyrolytic	0.291	pyrogenic+petrogenic
7	0.522	pyrolytic	0.005	petrogenic
8	0.529	pyrolytic	0	petrogenic
9	0.5	pyrolytic	0.079	petrogenic
10	0.545	pyrolytic	0.001	petrogenic
11	0.068	pyrolytic	0.015	petrogenic

Notes: ND – not detectable; Ant/(Ant+Phen) – anthracene/(anthracene+phenanthrene); BaA/(BaA+Chry) – benzo(a)pyrene/(benzo(a)pyrene+chrysene)

Table 3

Another indices value of PAHs and its origin source descriptions in soil samples at the studied Locations during the studied periods

Locations	Fl/Py	Description	Phen/Ant	Description	LMW/HMW	Description
1	0.5	petrogenic	0.8	pyrogenic	1.009	petrogenic
2	0.25	petrogenic	1.37	pyrogenic	0.323	pyrogenic
3	0.667	petrogenic	0.047	pyrogenic	0.949	pyrogenic
4	0.4	petrogenic	1	pyrogenic	0.799	pyrogenic
5	0.571	petrogenic	0.5	pyrogenic	0.248	pyrogenic
6	0.75	petrogenic	0.923	pyrogenic	1.656	petrogenic
7	1	petrogenic+pyrogenic	0.917	pyrogenic	2.333	petrogenic
8	1	petrogenic+pyrogenic	0.889	pyrogenic	0.219	pyrogenic
9	ND	–	1	pyrogenic	1.062	petrogenic
10	1	petrogenic+pyrogenic	0.833	pyrogenic	0.239	pyrogenic
11	0.667	petrogenic	13.725	pyrogenic	1.427	petrogenic

Notes: ND – not detected; Fl/Py – fluoranthene/pyrene; Phen/Ant – phenanthrene/anthracene; LMW/HMW – low molecular weight/high molecular weight

Station	%	#
1	4%	4.121
2	2%	2.342
3	3%	2.595
4	3%	2.66
5	7%	6.475
6	1%	1.36
7	7%	7.341
8	31%	30.707
9	1%	1.191
10	35%	35.042
11	6%	6.162

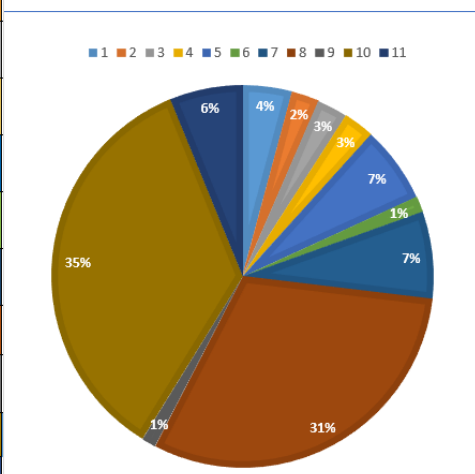


Fig. 2. The percentage of PAHs in different oil field is the percentage of PAHs in different oil field

The Comparison of The Current Concentrations of Surface Soil PAHs Compounds (ng-g⁻¹ dry weight) With Previous Studies at Basrah province

Table 4

4. Conclusions

Source	Study area	PAHs compounds (ng-g ⁻¹ dry weight)
[7]	West Qurna-2 Oil Field	1.125–5.906
[8]	Rumaila Oil Field	6600–4749300
[9]	West Qurna-1 Oil Field	1.335–3.592
[10]	Basrah province	0.6–112.57
[2]	Basrah province	531.21–5033.23
[11]	Industrial district Baiji – Kirkuk	94.9–416.3
[12]	Al-Ahdab oil field, Waset	19–855
[13]	Kirkuk oil refinery	10.92–26.92
[11]	Industrial district Baiji – Kirkuk	94.9–416.3
[14]	Nasiriyah oil field	0.003–73.462
[15]	Agriculture fields in Baghdad	0.21–30.2
[16]	Agriculture fields in Baghdad	99.1–322.6
[17]	AL-Nahrawan bricks factory, Baghdad	64910–245005
[18]	AL-Zubaidiya Thermal Power Plant, Baghdad	22790–45550
[19]	Kirkuk province	26.4–42.79
Current study	Seba Oil Field	268.64
	Safwan	152.72
	Majnoon Oil Field	169.19
	Ratawi Oil Field	173.4
	Bergezia Oil Field	422.1
	West Qurna1	478.58
	West Qurna2	88.7
	Shuaaba	2001.7
	South Rumaila	77.67
	North rumail	2284.27
Zubair Oil Field	401.69	

As a conclusion this Study gave a baseline of the pollution of PAHs compound which coming from Crude oil spills and gas burning of accompanied natural gas on the environment of Basrah oil field. According to their molecular weight, they were separated into two main groupings. The first group of compounds consisted of six compounds: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene. These light (low molecular weight) compounds have two to three fused aromatic rings. The first group includes nine chemicals: floranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b), benzo(k), benzo(a), benzo(a), indeno(1,2,3,c,d), and benzo(g,h,i)perylene. These heavy (high molecular weight) compounds included four or more fused aromatic rings. The percentage of PAHs in different oil field is where observed at highest percentage (35 %) at station 10 (North Rumala) while lower percentage (1.191 %) observed at station 9 (South Rumala). In this study we were able to obtain from this result could be used as a baseline data for further study in the futures.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

Financing

The research was performed without financial support.

Data availability

The manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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