



Polycyclic Aromatic Hydrocarbons (PAHs) in Soil of West Qurna-1 Oil Field Southern Iraq

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Abstract Distribution and source of Polycyclic Aromatic Hydrocarbons were determined seasonally in soil samples at ten stations in West Qurna-1 oil field Southern Iraq during the period from January 2018 to September 2018. The regional higher mean concentration of PAHs in soil samples at location 6 was (3.592 ng/g) during Winter and the lowest in Location 10 was (1.335 ng/g). The results of seasonal PAHs concentration in this study show that the lowest mean concentrations were recorded during Summer (12.176 ng/g), while the highest mean concentrations were recorded during Winter (2.820 ng/g). From the LMW/HMW, Phenanthrene/Anthracene and benzo (a) anthracene/benzo (a) anthracene+ chrysene ratios, the PAHs compound drive from pyrogenic sources, while Flouranthene / Pyrene Ratio and InP/(InP+BghiP) Ratio was pyrogenic+ petrogenic origin and petrogenic or pyrogenic and Ant/ (Ant+ Phen) Ratio was Pyrogenic.

Keywords PAH, Soil, West Qurna-1, oil field, Iraq

Introduction

PAHs (polycyclic aromatic hydrocarbons) exist in the environment and is distributed in both aquatic and terrestrial environments. PAHs can be both natural and anthropogenic origin. It can form by several pathways: biosynthesis, pyrogenic and petrogenic [1].

Petrogenic PAHs are relatively derived from petroleum and another fossil fuel containing PAHs. Diagenetic PAHs refer to PAHs formation from biogenic precursors, like plant terpenes, leading to the formation of compounds such as retene (methyl isopropyl phenanthrene or 1-methyl-7-isopropyl phenanthrene C₁₈H₁₈) and derivatives of phenanthrene and chrysene. A potential fourth source of PAHs is biogenic, i.e., purely from bacteria, fungi, plants or animals in sedimentary environments without any contributions from diagenetic processes, However, this source is not significant Polycyclic aromatic hydrocarbons (PAHs) are organic compounds consisting of two or more aromatic rings. Their presence in all environment compartments result from both natural processes such volcanic activity or forest fires and predominantly anthropogenic activities include waste incineration, burning wood, coal or garbage but also the operation of gasoline and diesel engines [2].

Polycyclic aromatic hydrocarbon (PAHs) are very dangerous substances because of their carcinogenic properties. It is important to know the features of PAHs transport and accumulation in soils, especially on agricultural lands. Aromatic hydrocarbons include monocyclic aromatics which their structure has at least one benzoid ring in their structure (e.g., benzene, toluene, and xylenes) and polycyclic aromatic hydrocarbons (PAHs), hydrocarbons are containing two or more fused benzene rings, which are one of the most essential classes of anthropogenic organic contaminants Crude and refined petroleum contains PAHs (i.e., petrogenic



PAHs). The PAHs are also produced by combustion of fossil fuel (coal and petroleum) and biomass (i.e., pyrogenic PAHs), there are also, natural sources of PAHs released to the environment [3].

They can transport over long distances in the atmosphere and deposit in faraway areas so that they are widely found in the environment [4]. There are large number of PAH compounds in the environment. sixteen compounds i.e. naphthalene, acenaphthylene, acenaphene, phenanthrene, fluorene, anthracene, fluoranthene, pyrene, chrysene, benzo (a) anthracene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, benzo (ghi) perylene, dibenzo (ah) anthracene, indeno1,2,3(cd) pyrene and coronene of the increased environmental and health interests. The physical, chemical and toxicological properties of these compounds are different and therefore, their evaluation in nature is required. The most grounded cancer-causing agents have been appeared to be benzo [a] anthracene, benzo [a] pyrene and dibenzo [ah] anthracene. They are multimedia contaminants, reported at elevated levels in several environmental examples i.e. dust, particulate matter, sludge and sewage of different region of the World [5]. Low molecular weight (LMW) PAHs, contains two or three fused rings, are more water soluble and volatile, along these lines they are more available, then high molecular weight (HMW) PAHs which containing four or more fused rings", hence (LMW) PAHs are more susceptible to different degradation processes. Long term exposure to hydrocarbon compounds can bring about different unsettling in human life in terms of comfort and health [6]. PAHs may create extent pollute all environmental matrices and raise toxicological, mutagenic and carcinogenic concerns. Inhalation of fine particles, skin contact and ingestion are the main routes of human exposure to PAHs. The determination of PAH concentrations in environmental matrices, for example, soil is important to characterize the levels of environmental contamination. PAHs may largely contaminate all environmental matrices and raise toxicological, mutagenic and carcinogenic concerns (IARC 2003). The main routes of human exposure to PAHs are inhalation of fine particles, dermal contact and ingestion. The determination of PAH concentrations in environmental matrices such as soil or plants is necessary to characterize the levels of environmental pollution and finally to assess the risk of human exposure. Thus, several studies have been conducted in the world on the evaluation of PAH concentrations in plants and soils [1,7-8].

The main objective of the present study in West Qurna-1 oil field investigate the seasonal and spatial distributions of PAH compounds, and determine the sources and origins of PAH pollution.

Material and Methods

Soil samples were collected seasonally during the period from January 2018 to September 2018 at ten stations in West Qurna-1 oil field at Basrah city (Fig.1). Samples were warped with aluminum foil then transferred to the laboratory for analysis.

The procedure which described by Grimalt and Olive [9] and Wang et al., [10] was used to extracted the hydrocarbons from soil. Twenty-five grams of soil were soxhlet extracted for 24 hours with 250ml methanol: benzen (1:1). Elemental sulfur was removed from the extracts using activated elemental copper in order to avoid sulfur interferences when using gas chromatography. The extracts were then fractionated into aliphatic and aromatic hydrocarbons by chromatography column. The column was prepared by slurry packing 10g of silica (100-200 mesh), followed by 10g 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 finally 1 g of anhydrous sodium sulphate was added to the surface to avoid disturbance of the top layer when pouring the solvent. The extract was then applied to the head of the column and eluted 25 ml of benzene to yield the aromatic hydrocarbons. The aromatic fractions were concentrated on a rotary evaporator, transferred to a vial, and the volume was adjusted to 1 ml exactly using a stream of N₂. An aliquot of 1 µl of extract of aromatic hydrocarbons was subjected to analysis by an allegiant capillary gas chromatography with flam ionization detector (FID). Column (model Agilent 19091J-101HP-5 5% phenyl Methyl silicone with dimensions for PAHs the temperature of column was held at 80 °C for 2 minutes then rate 8 °C /minute to 280°C for 12 min. The individual of PAHs was identified based on the retention time of an authentic mixed standard procured from Supelco, USA. The concentrations and PAHs compounds were calculated based on the standard calibration curve of corresponding standard compounds. 80 % to 92 % are the range of recovery assays for PAHs compounds. Standard deviation for the method was less than 10 % based on replicate analysis. Great care was taken to avoid contamination of the samples throughout the



analytical procedure. All solvents were distilled twice before use; glassware was rinsed with distilled water and heated in an oven at 250 °C for 24 hours. However, procedural blanks consisting of all reagents and glassware used during the analysis were periodically determined which had shown no detectable interference.

Ratios of (LMW-PAHs) to (HMW-PAHs), values less than one are attributed to pyrogenic sources and values greater than one indicate petrogenic origins from crude oil and their derivatives [11].

LMW= Sum of concentrations of light PAHs (2-3 rings).

HMW= Sum of concentrations of heavy PAHs (4 rings and more).

If the value of $BaA / (BaA + Chr)$ is less than (0.2), it indicates that the source of PAHs is Petrogenic. If its value is between 0.2-0.35, this indicates that the source of PAHs either Petrogenic or Pyrogenic, but if its value is greater than 0.35 the source of PAHs is Pyrogenic [12-14].

If value of this ratio is less than (0.2), the source of PAHs is Petrogenic, if the value of the PAHs is 0.2-0.5, this indicates either Petrogenic or Pyrogenic origins. If the value is higher than 0.5, the source of the PAHs is Pyrogenic [12-14].

If the value of (FI/Py) is less than one, the source of the PAHs is Petrogenic, while if the value of (FI/Py) is greater than the number 1, the source of PAHs is Pyrogenic [15-16]. The ratio values higher than ten, the hydrocarbons are petrogenic in origin. When the ratio values less than ten (10) show that the hydrocarbons are pyrogenic in origin [16-18].

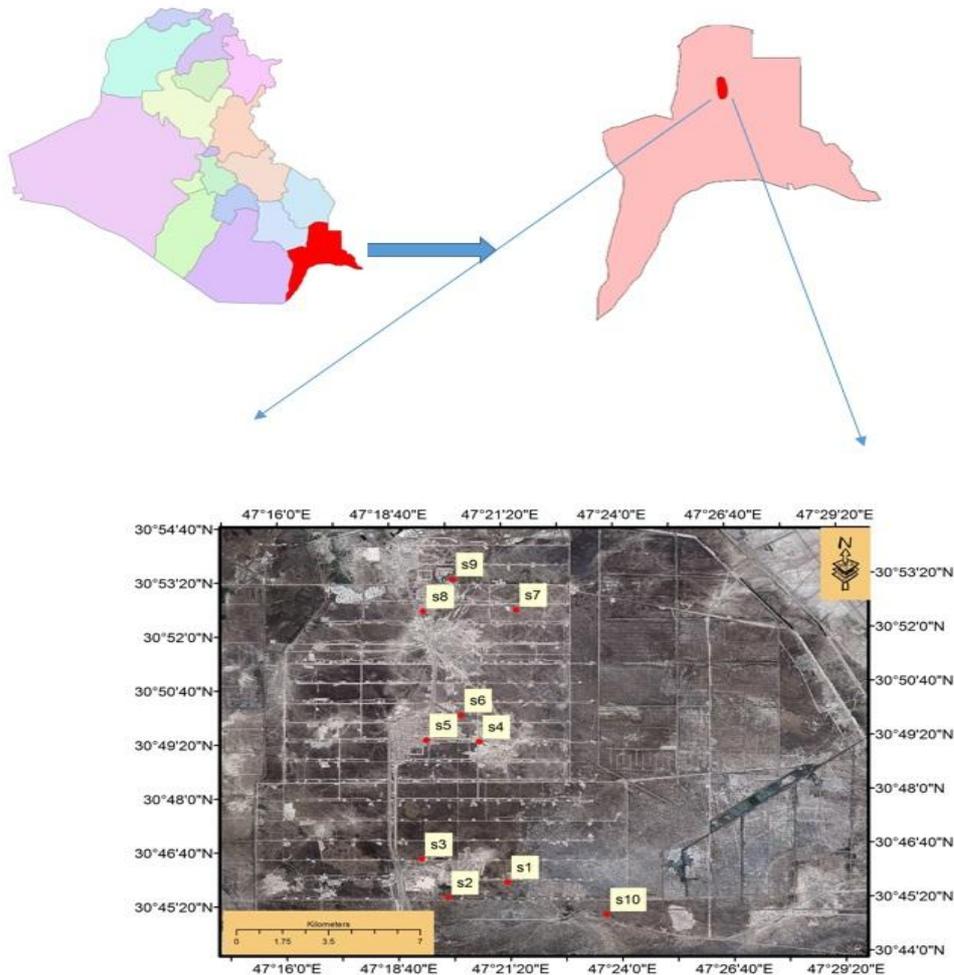


Figure 1: The study area

Results

The total concentrations of PAHs in soil samples at ten Locations are range as following: Location 1 from 2.260 ng/g during Summer to 2.789 ng/g during Winter. In Location 2 from 2.366 ng/g during Summer to 2.584



ng/g during Autumn. While in Location 3 from 2.063ng/g during Summer to 2.405 ng/g during Winter. Whereas in Location 4 from 1.979 ng/g during Summer to 2.687 ng/g during Winter. In Location 5 from 2.210 ng/g during Summer to 2.393 ng/g during Spring. Location 6 from 2.467 ng/g during Autumn to 3.592 ng/g during Winter,

Location 7 from 2.542 ng/g during Summer to 3.427 ng/g during Winter, Location 8 from 2.334 ng/g during Summer to 3.052 ng/g during Winter, Location 9 from 2.384 ng/g during Summer to 3.208ng/g during Winter and Location 10 from 1.335 ng/g during Summer to 2.331 ng/g during Winter Tables (1-4).

The highest concentrations of total PAHs in soil are recorded at Location 6 (3.592 ng/g) dry weight during Winter, while the lowest concentrations are recorded at Location 10 (1.335 ng/g) dry weight during Summer Tables (1-4).

The study of Seasonal variations of total PAHs showed that, the highest of seasonal mean concentrations were detected during Winter was at Autumn season while lower concentration noticed during Summer season (Table 5).

Table 1: Spatial Concentrations of Polycyclic Aromatic Hydrocarbons (ng/g) dry weight in Soil of west Qurna- 1 Oil Field during winter season 2018

PAHs compounds	Location									
	1	2	3	4	5	6	7	8	9	10
Naphthalene	0.074	0.102	0.025	0.017	0.024	0.032	0.012	0.032	0.028	0.017
Acenaphthylene	0.216	0.021	0.025	0.024	0.017	0.031	0.054	0.038	0.021	0.102
Acenaphene	0.120	0.112	0.047	0.110	0.054	0.074	0.153	0.067	0.121	0.021
Fluorene	0.271	0.217	0.218	0.329	0.174	0.271	0.318	0.260	0.318	0.603
Phenanthrene	0.142	0.122	0.326	0.581	0.283	0.173	0.185	0.521	0.437	0.327
Anthracene	0.310	0.327	0.102	0.126	0.630	0.421	0.438	0.236	0.520	0.372
Fluoranthene	0.048	0.123	0.053	0.625	0.236	0.246	0.260	0.327	0.160	0.016
Pyrene	0.376	0.160	0.172	0.164	0.233	0.173	0.317	0.235	0.248	0.248
Benzo(a)anthracene	0.365	0.283	0.315	0.152	0.112	0.215	0.292	0.262	0.123	0.123
Chrysene	0.042	0.214	0.126	0.027	0.127	0.221	0.547	0.285	0.430	0.043
Benzo(b)fluoranthene	0.151	0.025	0.132	0.036	0.181	0.172	0.216	0.210	0.085	0.021
Benzo(k)fluoranthene	0.262	0.315	0.341	0.134	0.018	0.219	0.490	0.327	0.422	0.320
Benzo(a)pyrene	0.013	0.104	0.115	0.032	0.024	0.035	0.028	0.023	0.014	0.019
Indo(1,2,3-cd)pyrene	0.091	0.083	0.040	0.108	0.069	0.095	0.096	0.085	0.058	0.078
Dibenzoanthracene	0.222	0.104	0.174	0.155	0.098	0.262	0.022	0.100	0.140	0.011
Benzo(g,h,i)perylene	0.086	0.055	0.194	0.054	0.067	0.052	0.066	0.044	0.083	0.010
Total	2.789	2.367	2.405	2.687	2.347	3.592	3.427	3.052	3.208	2.331

Table 2: Spatial Concentrations of Polycyclic Aromatic Hydrocarbons (ng/g) dry weight in Soil of west Qurna- 1 Oil Field during spring season 2018

PAHs compounds	Location									
	1	2	3	4	5	6	7	8	9	10
Naphthalene	0.217	0.074	0.029	0.183	0.128	0.121	0.074	0.161	0.283	0.047
Acenaphthylene	0.181	0.141	0.117	0.120	0.151	0.053	0.129	0.211	0.127	0.041
Acenaphene	0.261	0.204	0.217	0.161	0.240	0.144	0.261	0.253	0.121	0.015
Fluorene	0.164	0.120	0.140	0.122	0.255	0.221	0.351	0.140	0.238	0.120
Phenanthrene	0.214	0.232	0.154	0.232	0.154	0.133	0.210	0.120	0.221	0.117
Anthracene	0.165	0.230	0.202	0.186	0.271	0.248	0.132	0.230	0.311	0.045
Fluoranthene	0.162	0.216	0.215	0.277	0.087	0.223	0.280	0.211	0.265	0.076
Pyrene	0.175	0.117	0.218	0.121	0.125	0.122	0.111	0.187	0.194	0.065
Benzo(a)anthracene	0.220	0.217	0.116	0.202	0.211	0.233	0.265	0.261	0.282	0.115
Chrysene	0.110	0.023	0.120	0.021	0.032	0.044	0.121	0.162	0.032	0.075



Benzo(b) fluoranthene	0.219	0.143	0.054	0.125	0.164	0.143	0.162	0.107	0.159	0.110
Benzo(k) fluoranthene	0.176	0.212	0.203	0.058	0.118	0.216	0.173	0.149	0.109	0.254
Benzo(a) pyrene	0.116	0.271	0.165	0.210	0.128	0.142	0.251	0.119	0.290	0.113
Indo(1,2,3-cd) pyrene	0.021	0.042	0.065	0.072	0.102	0.121	0.051	0.072	0.110	0.073
Dibenzoanthracene	0.211	0.157	0.222	0.131	0.150	0.216	0.246	0.315	0.122	0.114
Benzo(g,h,i) perylene	0.128	0.064	0.153	0.082	0.077	0.122	0.108	0.211	0.104	0.063
Total	2.740	2.463	2.390	2.303	2.393	2.502	2.925	2.909	2.958	1.443

Table 3: Spatial Concentrations of Polycyclic Aromatic Hydrocarbons (ng/g) dry weight in Soil of west Qurna- 1 Oil Field during summer season 2018

PAHs compounds	Location									
	1	2	3	4	5	6	7	8	9	10
Naphthalene	0.203	0.073	0.027	0.159	0.119	0.120	0.093	0.152	0.219	0.044
Acenaphthylene	0.165	0.128	0.104	0.111	0.128	0.051	0.094	0.203	0.110	0.042
Acenaphene	0.245	0.200	0.197	0.138	0.218	0.132	0.238	0.231	0.119	0.013
Fluorene	0.152	0.109	0.117	0.110	0.217	0.209	0.329	0.118	0.215	0.117
Phenanthrene	0.211	0.220	0.139	0.210	0.132	0.126	0.208	0.118	0.210	0.113
Anthracene	0.153	0.218	0.178	0.175	0.237	0.223	0.120	0.218	0.200	0.043
Fluoranthene	0.153	0.218	0.200	0.164	0.224	0.217	0.116	0.218	0.205	0.042
Pyrene	0.149	0.113	0.199	0.108	0.111	0.109	0.105	0.176	0.138	0.062
Benzo(a) anthracene	0.218	0.205	0.102	0.178	0.206	0.220	0.235	0.238	0.219	0.112
Chrysene	0.107	0.096	0.094	0.019	0.028	0.023	0.119	0.134	0.029	0.068
Benzo(b) fluoranthene	0.209	0.111	0.049	0.112	0.121	0.129	0.138	0.100	0.108	0.107
Benzo(k) fluoranthene	0.149	0.188	0.177	0.054	0.103	0.206	0.147	0.123	0.098	0.244
Benzo(a) pyrene	0.108	0.253	0.148	0.208	0.102	0.119	0.228	0.112	0.228	0.102
Indo(1,2,3-cd) pyrene	0.011	0.038	0.058	0.066	0.097	0.119	0.047	0.064	0.098	0.063
Dibenzoanthracene	0.194	0.139	0.207	0.092	0.105	0.189	0.225	0.276	0.091	0.105
Benzo(g,h,i) perylene	0.016	0.057	0.127	0.075	0.062	0.095	0.100	0.203	0.097	0.058
Total	2.260	2.366	2.063	1.979	2.210	2.287	2.542	2.334	2.384	1.335

Table 4: Spatial Concentrations of Polycyclic Aromatic Hydrocarbons (ng/g) dry weight in Soil of west Qurna- 1 Oil Field during Autumn season 2018

PAHs compounds	Location									
	1	2	3	4	5	6	7	8	9	10
Naphthalene	0.069	0.097	0.020	0.014	0.094	0.119	0.186	0.182	0.021	0.012
Acenaphthylene	0.211	0.014	0.118	0.019	0.013	0.024	0.143	0.031	0.019	0.092
Acenaphene	0.116	0.154	0.165	0.095	0.043	0.052	0.137	0.052	0.117	0.016
Fluorene	0.251	0.211	0.213	0.297	0.155	0.242	0.101	0.241	0.295	0.329
Phenanthrene	0.137	0.216	0.300	0.521	0.247	0.162	0.164	0.249	0.322	0.310
Anthracene	0.295	0.302	0.097	0.116	0.422	0.403	0.211	0.221	0.399	0.348
Fluoranthene	0.031	0.217	0.148	0.612	0.215	0.232	0.157	0.294	0.149	0.011
Pyrene	0.352	0.146	0.163	0.137	0.210	0.144	0.178	0.264	0.225	0.210
Benzo(a) anthracene	0.356	0.273	0.289	0.111	0.094	0.202	0.173	0.243	0.110	0.095
Chrysene	0.022	0.195	0.012	0.117	0.114	0.297	0.295	0.254	0.394	0.033
Benzo(b) fluoranthene	0.137	0.019	0.128	0.102	0.127	0.245	0.199	0.193	0.061	0.015
Benzo(k) fluoranthene	0.243	0.298	0.321	0.120	0.112	0.192	0.266	0.310	0.398	0.093



fluoranthene										
Benzo(a)pyrene	0.011	0.135	0.012	0.022	0.121	0.028	0.212	0.116	0.010	0.014
Indo(1,2,3-cd)pyrene	0.077	0.068	0.133	0.089	0.153	0.064	0.171	0.166	0.049	0.040
Dibenzoanthracene	0.196	0.197	0.150	0.010	0.179	0.023	0.217	0.093	0.127	0.010
Benzo(g,h,i)perylene	0.067	0.042	0.062	0.038	0.055	0.038	0.052	0.032	0.061	0.011
Total	2.571	2.584	2.331	2.420	2.354	2.467	2.862	2.941	2.757	1.639

Table 5: Seasonal variations of Polycyclic Aromatic Hydrocarbons (ng/g) with mean in West Qurna1 oil field

Locations	Winter	Spring	Summer	Autumn	Sp. mean	±SD
1	2.789	2.740	2.260	2.571	2.590	0.238
2	2.367	2.463	2.366	2.584	2.445	0.111
3	2.405	2.390	2.063	2.331	2.297	0.159
4	2.687	2.303	1.979	2.420	2.347	0.289
5	2.347	2.393	2.210	2.354	2.326	0.079
6	3.592	2.502	2.287	2.467	2.712	0.594
7	3.427	2.925	2.542	2.826	2.930	0.368
8	3.052	2.909	2.334	2.941	2.848	0.322
9	3.208	2.958	2.384	2.757	2.826	0.348
10	2.331	1.443	1.335	1.639	1.687	0.447
S. Mean	2.820	2.502	2.176	2.489	-	-

Sp. mean= Spatial mean, S. Mean= seasonal mean.

Polycyclic Aromatic Hydrocarbons (PAH) Indices

The Fluoranthene / Pyrene Ratio is ranged from (0.127) at Location 2 in Winter to (3.810) at Location 4 in Winter (Table 6). Phenanthrene /Anthracene ratio is ranged from (0.373) at Location 2 in Winter to (4.491) at Location 4 in Autumn season (Table 6).LMW/HMW ratio ranges from (0.363) at Location 10 in Spring to (2.080) at Location 10 in Autumn (Table 6). Ant / (Ant+Phen) ratio is ranged from (0.178) at Location4 in Winter to (0.728) at Location 2 in Winter (Table 7). BaA / (BaA+Chry) ratio is ranged from (0.218) at location 9 in Autumn to (0.960) at location 3 in Autumn (Table 7). InP / (InP+BghiP) ratio is ranged from (0.103) at Location 1in Autumn to (0.886) at Location10 in Winter (Table 7).

Table 6: Pollution indices values of PAHs and its origin source descriptions in soil samples at the studied Locations during the studied periods

Locations	Seasons	Fl/Py	Description	Phen/Ant	Description	LMW /HMW	Description
1	Winter	0.127	petrogenic	0.458	Pyrogenic	0.684	pyrogenic
	Spring	0.925	petrogenic	1.296	pyrogenic	0.781	pyrogenic
	Summer	1.020	pyrogenic	1.379	pyrogenic	0.859	pyrogenic
	Autumn	0.713	petrogenic	0.464	pyrogenic	0.723	pyrogenic
2	Winter	0.768	petrogenic	0.373	pyrogenic	0.617	pyrogenic
	Spring	1.846	pyrogenic	1.008	pyrogenic	0.684	pyrogenic
	Summer	0.964	petrogenic	1.009	pyrogenic	0.668	pyrogenic
	Autumn	1.445	pyrogenic	0.715	pyrogenic	0.625	pyrogenic
3	Winter	0.308	petrogenic	3.196	pyrogenic	0.588	pyrogenic
	Spring	0.986	petrogenic	0.762	pyrogenic	0.561	pyrogenic
	Summer	0.587	petrogenic	0.780	pyrogenic	0.559	pyrogenic
	Autumn	0.429	petrogenic	3.797	pyrogenic	0.535	pyrogenic
4	Winter	3.810	pyrogenic	4.611	pyrogenic	0.798	pyrogenic
	Spring	2.289	pyrogenic	1.247	pyrogenic	0.717	pyrogenic
	Summer	1.018	pyrogenic	1.200	pyrogenic	0.839	pyrogenic
	Autumn	2.167	pyrogenic	4.491	pyrogenic	0.782	pyrogenic
5	Winter	1.012	pyrogenic	0.449	pyrogenic	1.014	petrogenic
	Spring	0.696	petrogenic	0.568	pyrogenic	1.004	petrogenic
	Summer	1.954	pyrogenic	0.556	pyrogenic	0.906	pyrogenic
	Autumn	0.738	petrogenic	0.585	pyrogenic	0.705	pyrogenic
6	Winter	1.012	pyrogenic	0.410	pyrogenic	0.594	pyrogenic



7	Spring	1.827	pyrogenic	0.536	pyrogenic	0.481	pyrogenic
	Summer	1.917	pyrogenic	0.565	pyrogenic	0.603	pyrogenic
	Autumn	1.680	pyrogenic	0.401	pyrogenic	0.683	pyrogenic
	Winter	1.421	pyrogenic	0.422	pyrogenic	0.483	pyrogenic
8	Spring	2.522	pyrogenic	1.590	pyrogenic	0.616	pyrogenic
	Summer	3.133	pyrogenic	1.733	pyrogenic	0.741	pyrogenic
	Autumn	0.567	petrogenic	0.777	pyrogenic	0.508	pyrogenic
	Winter	1.391	pyrogenic	1.360	pyrogenic	0.638	pyrogenic
9	Spring	1.128	pyrogenic	0.521	pyrogenic	0.621	pyrogenic
	Summer	0.670	petrogenic	0.541	pyrogenic	0.632	pyrogenic
	Autumn	0.912	petrogenic	1.126	pyrogenic	0.496	pyrogenic
	Winter	0.645	petrogenic	0.840	pyrogenic	0.817	pyrogenic
10	Spring	1.365	pyrogenic	0.710	pyrogenic	0.780	pyrogenic
	Summer	1.557	pyrogenic	1.050	pyrogenic	0.818	pyrogenic
	Autumn	1.311	pyrogenic	0.807	pyrogenic	0.740	pyrogenic
	Winter	0.064	petrogenic	0.879	pyrogenic	1.622	petrogenic
	Spring	1.169	pyrogenic	2.600	pyrogenic	0.363	pyrogenic
	Summer	1.88	pyrogenic	2.627	pyrogenic	0.386	pyrogenic
	Autumn	1.566	pyrogenic	0.890	pyrogenic	2.080	petrogenic

Table 7: PAHs pollution indices values and its origin source descriptions in soil samples at the studied Locations during the studied periods

Locations	Seasons	Ant/(Ant+Phen)	Description	BaA/(BaA+Chry)	Description	InP/(InP+BghiP)	Description
1	Winter	0.685	Pyrolytic	0.896	pyrogenic	0.514	Pyrogenic
	Spring	0.435	Pyrolytic	0.666	pyrogenic	0.140	Petrogenic
	Summer	0.420	Pyrolytic	0.670	pyrogenic	0.407	Petrogenic pyrogenic or
2	Autumn	0.682	Pyrolytic	0.941	pyrogenic	0.103	Petrogenic
	Winter	0.728	Pyrolytic	0.5.69	pyrogenic	0.601	pyrogenic
	Spring	0.497	Pyrolytic	0.904	pyrogenic	0.396	Petrogenic pyrogenic or
3	Summer	0.497	Pyrolytic	0.681	pyrogenic	0.400	Petrogenic pyrogenic or
	Autumn	0.583	Pyrolytic	0.583	pyrogenic	0.618	Pyrogenic
	Winter	0.238	Pyrolytic	0.923	pyrogenic	0.298	Petrogenic pyrogenic or
4	Spring	0.657	Pyrolytic	0.491	pyrogenic	0.298	Petrogenic pyrogenic or
	Summer	0.561	Pyrolytic	0.520	pyrogenic	0.313	Petrogenic pyrogenic or
	Autumn	0.244	Pyrolytic	0.960	pyrogenic	0.682	Pyrogenic
5	Winter	0.178	Pyrolytic	0.849	pyrogenic	0.666	pyrogenic
	Spring	0.444	Pyrolytic	0.905	pyrogenic	0.467	Pyrogenic petrogenic or
	Summer	0.454	Pyrolytic	0.903	pyrogenic	0.468	Petrogenic pyrogenic or
6	Autumn	0.182	Pyrolytic	0.486	pyrogenic	0.700	Pyrogenic
	Winter	0.690	Pyrolytic	0.468	pyrogenic	0.507	pyrogenic
	Spring	0.637	Pyrolytic	0.868	pyrogenic	0.569	pyrogenic
7	Summer	0.642	Pyrolytic	0.880	pyrogenic	0.610	Pyrogenic
	Autumn	0.630	Pyrolytic	0.451	pyrogenic	0.735	Pyrogenic
	Winter	0.708	Pyrolytic	0.493	pyrogenic	0.646	pyrogenic
8	Spring	0.650	Pyrolytic	0.841	pyrogenic	0.497	Petrogenic pyrogenic or
	Summer	0.38	Pyrolytic	0.905	pyrogenic	0.556	Pyrogenic
	Autumn	0.713	Pyrolytic	0.404	pyrogenic	0.627	Pyrogenic



7	Winter	0.700	Pyrolytic	0.348	Petrogenic or pyrogenic	0.592	pyrogenic	
	Spring	0.385	Pyrolytic	0.686	Pyrogenic	0.331	Petrogenic or pyrogenic	or
	Summer	0.365	Pyrolytic	0.663	pyrogenic	0.319	Petrogenic or pyrogenic	or
	Autumn	0.562	Pyrolytic	0.348	Petrogenic or pyrogenic	0.766	Pyrogenic	
8	Winter	0.311	Pyrolytic	0.478	Pyrogenic	0.658	pyrogenic	
	Spring	0.657	Pyrolytic	0.617	Pyrogenic	0.254	Petrogenic or pyrogenic	or
	Summer	0.648	Pyrolytic	0.639	pyrogenic	0.239	Petrogenic or pyrogenic	or
	Autumn	0.470	Pyrolytic	0.488	pyrogenic	0.838	Pyrogenic	
9	Winter	0.543	Pyrolytic	0.222	Petrogenic or pyrogenic	0.411	Petrogenic or pyrogenic	or
	Spring	0.584	Pyrolytic	0.898	Pyrogenic	0.342	Petrogenic or pyrogenic	or
	Summer	0.487	Pyrolytic	0.883	pyrogenic	0.502	Pyrogenic	
	Autumn	0.554	Pyrolytic	0.218	Petrogenic or pyrogenic	0.445	Petrogenic or pyrogenic	or
10	Winter	0.532	Pyrolytic	0.740	pyrogenic	0.886	pyrogenic	
	Spring	0.277	Pyrolytic	0.605	pyrogenic	0.536	pyrogenic	
	Summer	0.275	Pyrolytic	0.595	pyrogenic	0.520	Pyrogenic	
	Autumn	0.528		0.742	pyrogenic	0.784	Pyrogenic	

Discussion

The predominant light PAHs compounds are Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, and Anthracene while the dominant heavy PAHs compounds are Floranthene, Pyrene, Benzo(a)Pyrene, Benzo(a)anthracene, Benzo(k)flouranthene. Benzo [a] anthracene and benzo [a] pyrene are the most effective carcinogens have been found [5].

At all Locations along the period of study observed that HMW-PAHs are more than LMW-PAHs, this may be attributed to the molecular weight. Differences in degradation processes in both low and high molecular weight PAHs because of wide group of microorganisms including fungi, algae and bacteria. In any case, bacteria play the most important role in completion of mineralization. Lower molecular weight PAHs such as naphthalene and phenanthrene degrade rapidly, but higher molecular weight PAHs such as pyrene, fluoranthene, benzo(a)anthracene and benzo(a)pyrene are more recalcitrant [2, 19]. In expansion to that the low molecular weight PAHs such as naphthalene has the highest vapor pressure of PAHs, therefore volatilization in environments is probably the most important removal mechanism for these compounds [20-21].

The results of seasonal PAHs at the present study show a highest concentration of PAHs is in Winter at Location 7 and the lowest in Summer at Location 10.

The oil industry holds a major potential of hazards for the environment, and may impact it at different levels: air, water, soil, and consequently all living beings on our area. The most widespread and dangerous consequence of oil and gas industry activities is the pollution which is associated with all activities throughout all stages of oil and gas production, from exploratory activities to refining [22].

Results of seasonal PAHs mean concentrations in this study show that the lowest concentrations recorded during Summer (2.176 ng/g), while the highest concentrations recorded during winter, the seasonal mean concentration arrange as following:

Winter >Spring>Autumn>Summer.

This may be attributed to the climatic condition effect by photo-oxidation, volatilization and high degradation during the hot season. Increasing the evaporation rate and also affect the biodegradation during Summer because of the high temperature. Generally, the rate of biodegradation decreases with decreasing of temperature and vice versa, so that the highest degradation rates generally occurs in the range 20 to 30 °C in the environments.



Because of higher energy consumption for heating and increase hydrocarbon compound input to environment with run off during Winter season, elevated levels of them during Winter may be attributed to their in precipitation which are significantly higher in Winter than in Summer. In addition, during Winter, because of lowering in temperature the evaporation rate decreases, also biodegradation rate decreased during Winter [23-25].

The effect of TOC and grain size on the PAHs concentrations in soil is investigated in the present study. The variation in % TOC among the Locations can be due to different organic matter sources and soil. A significant positive correlation between TOC% and total PAHs in the soil are found at this study ($r=0.888$, $P<0.01$). This result was in agreement with [22, 26-27]. The importance of sedimentary organic matter on the PAHs partitioning in sediments have been well documented by Chiou *et al.*, [28]. They found that the high partitioning of PAHs to sedimentary organic matter is mainly due to the significant aromatic fraction of the organic matter. They are considered the sedimentary organic matter as a natural “heterogeneous polymer” where PAHs interact more favorably with the aromatic regions.

According to the LMW /HMW ratio, the main source of PAHs in soil of West Qurna-1 oil field is pyrogenic origin, depending on the variation in the concentrations of carbazol, anthracene, chrysene and floranthene which controls the ratio of LMW/HMW. Results of the present study are in agreement with Al-Khatib [25] who found that the hydrocarbons source in Al-Howaiza Marsh is pyrogenic origin. Also, the present result was in agreement with Al-Khion [18] who found that PAHs compounds in the sediments of Iraqi Coast region is pyrogenic origin source according to ratio <1 and petrogenic origin according to ratio >1 .

Phenanthrene /Anthracene ratio is used by many authors [6, 17-18, 25-27, 29] to detect the origin of PAHs compounds in sediments. The present study shows Phenanthrene / Anthracene Ratio tend to be pyrogenic origins. Results of the present study are in agreement with Al-Mahana [26] who found that the hydrocarbons source in Al-Qurna is pyrogenic origin. That gives indication that the source of these compounds is a result of combustion of fossil fuels.

According the ratio value, the main source of PAHs in soil is pyrogenic+ petrogenic origin. According to the ratio values, the source of PAHs in soil is pyrogenic (combustion sources) and petrogenic (petroleum contaminations).

According to the ratio values, the source of PAHs in soil is pyrogenic, Results of the present study are in agreement with Al-Mahana [26] who found that the hydrocarbons source in Al-Qurna is pyrogenic origin.

According to the ratio values, the source of PAHs in soil is petrogenic or pyrogenic.

Conclusion

This study gave an idea about the source and distribution of PAH in soil of West quarna-1 oil field, the PAH compound divided in two pattern Low and High molecular weight, the sources of them petrogenic or pyrogenic.

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