Hydrocarbons in Soil from Basra Oil-Rich Governorate

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ABSTRACT

Basra is a rich-oil region; its soil is expected to be contaminated with petroleum hydrocarbons. However, there is no previous study that has estimated the levels of hydrocarbons in Basra soil. After 2003 numerous operations by several international oil companies are underway. Therefore, the determination of background levels of petroleum hydrocarbons is a priority from environmental point of view. The present study was carried out to determine the distribution and seasonal variations of petroleum hydrocarbons in ten sites in Basra Governorate, southern Iraq. The results obtained in this study can service as baseline for future environmental impact assessment of oil operations.

Keywords: Basra, Oil Pollution, Petroleum Hydrocarbons, PAHs, Impact Assessment

1. INTRODUCTION

Hydrocarbons are considered as an important class of environmental pollutants especially in areas where oil is found. This may be due to anthropogenic activities such as spillage, leakages and handling of crude oils (Farrell-Jones, 2003; Butler et al., 1984). Soils can also retain relatively low amounts of hydrocarbons from natural sources "biogenic" such as higher plants. The concentrations of hydrocarbons in soil are strongly related to the sorbed organic matter (Zhang et al., 2012; Whittaker et al., 1999), similarly the present study has confirmed. On the other hand, hydrocarbons may be removed from soil via several processes such as volatilization, photo-oxidation, chemical reactions, leaching and biodegradation (Grimalt and Olive, 1993). Pending on environmental conditions, some of these processes may take very long time and thus portion of these compounds will remain in soil and become more resistant (Barakat et al., 2001). Increasing hydrocarbons levels in the environment can cause pollution to the natural resources (Buddhadasa et al., 2002). On the other hand, poly-nuclear aromatic hydrocarbons considered major carcinogenic component that can cause serious health problems (Apitz and Meyers-Schulte, 1996; API, 2001; Askari and Pollard, 2005). High levels of hydrocarbons are expected to be encountered in several locations within Basra Governorate. In addition to the numerous oil operations, there are additional sources of hydrocarbons to this region such as industries, power generation and gas productions. Inadequate waste management suggests high levels of hydrocarbons residues in Basra soil, especially within the industrial zone. The main objectives of this study are to determine the baseline hydrocarbon concentrations in Basra soil and point their main sources in an attempt to correlate their impact upon surrounding areas.

2. MATERIALS AND METHODS

Ten sampling locations were selected across Basra Governorate based upon vicinity to oil operations, industrial sites and urban areas. Thus, Basra station is mainly affected by electrical generating plants and units. Al-Rumayllah and Al-Seeba areas host the largest oil refineries. Fao port is station suspected to be heavily influenced by oil exportation. The rest stations are mainly urban areas

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including: Al-Qurna, Garmett Ali, Al-Shiabah, Abu Kaseeb, Saffwan and Um Qasir. Replicate soil samples were collected using hand auger from each station during 2009 to account for winter and summer season.

Samples were wrapped in aluminum foil and placed in sterilized containers and kept in the laboratory deep freeze. The samples then were freeze-dried, grounded finely by agate mortar and sieved through a 62μ stainless steel sieve. Hydrocarbons were extracted from soil followed the procedure described by Grimalt and Olive (1993) and Tuteja *et al.* (2011). The extracts were divided into two portions. The first portion was used to determine total petroleum hydrocarbons using a Shimadzu RF-540 spectroflurometer. The extract volume was reduced using a rotary evaporator to 10 mL and then sabonified for 2 h with a solution of 4N KOH in 1:1 methanol: Benzene and then dried by anhydrous Na_2SO_4 and concentrated by a stream of nitrogen. Petroleum hydrocarbons were quantified by measuring the emission intensity at 360 nm, with excitation set at 310 nm and monochromatic slits of 10 nm. The second portion of the extract was used to determine the aliphatic (n-alkanes) and aromatic hydrocarbons using a Perkin-Elmer sigma 300 gas chromatograph. Prior to GC analysis the extracts were cleaned by passing them through column filled with 8g of 5% deactivated alumina (100-200 mesh) on the top and silica (100-200 mesh) in the bottom. The samples then were eluted by 50 mL n-hexane (aliphatic fraction) followed by 50 mL of benzene (aromatic fraction). Both fractions were reduced to suitable volume and subjected to GC analysis. Helium gas was used as a carrier gas with a linear velocity of 1.5 mL min^{-1}. The operating temperatures for detector and injector were 350°C and 320°C, respectively. The silica capillary column was operated under initial, final and rate temperatures that programmed as follows: Initial temperatures were 60°C for aliphatic fraction for 4 min and 70°C for aromatic fraction for 0 min, while final temperatures were 280°C for aliphatic fraction and 300°C for aromatic fraction for 30 min and rate was 4°C/min for both aliphatic and aromatic fractions. Quantification of peaks and identification of hydrocarbons were done by a Perkin-Elmer computing integrator model LC-100. The Unresolved Complex Mixture (UCM) was measured using planimetry. The Odd and Even n-alkane Predominance Index (OEPI) and the Carbon Preference Indices (CPI) were used to indicate the general source of hydrocarbons whether their origin was biogenic or anthropogenic (API, 2001; Askari and Pollard, 2005). Pristane/Phytane ratio, Pristane/C_{17} and Phytane/C_{18} and the Unresolved Complex Mixture index (UCM) were used as indicators of petroleum contamination (API, 2001; Barakat *et al.*, 2001) and to estimate the degree of bacterial degradation (XiaoPing *et al.*, 2007).

3. RESULTS AND DISCUSSION

The concentrations of total hydrocarbons in μg/g and poly-nuclear aromatic hydrocarbons in ng/g in the Basra soil samples are exhibited in **Fig. 1 and 2** and listed in **Table 1**. The results of the preset work have clearly indicated that there is a significant differences in total hydrocarbon concentrations among industrial sites as oppose urban areas. As expected the rather elevated concentrations are always encountered in the industrial sites. An exception to this is Al-Seba site, where low levels of hydrocarbons were found despite the fact that Abadan Refinery lies across the river. The average concentrations of the total hydrocarbons in the urban sites were usually low, except in Al-Shiabah that shows relatively high concentrations mainly due to the impact of the oil refiner in Al-Rumella. However, the highest total hydrocarbons concentration was 38.8 μg g^{-1} found in Al-Rumayllah station where the lowest concentration was 13.0 μg g^{-1} found in Karmatt Ali station. Most of the soil samples collected during the study period showed emission peaks in the range of 340-380 nm, which indicate presence of highly condensed aromatic ring that typically found in crude oil. Generally, the results show that the total hydrocarbons concentrations were higher in winter than that recorded for summer. This may be attributed mainly to temperature drop in winter and thus reduce hydrocarbon evaporation rate (Hamme *et al.*, 2003; Wang and Fingas, 2003); however, these variation were not statistically insignificant (p>0.005). Among the measured polynuclear aromatic hydrocarbons, benzo (a) pyrene was represented in high concentrations in the urban sites, while both benzo (a) pyrene and chrysene were found in high concentrations in the industrial sites (**Fig. 2**). The chromatographic distributions of carbon chain lengths of the average n-alkanes concentrations indicate different variations of peaks among the studied locations; however, these peaks exhibit a significant n-alkanes profile consisting of a uni-model distribution centered at C_{21}-C_{26} (**Fig. 3**). The distribution of total average n-alkanes concentrations in the urban stations ranged from 9.2 μg g^{-1} ($\pm$SE 1.3) in Garmat Ali to 15.7 μg g^{-1} ($\pm$SE 1.2) in Um Qasir, while their total average in the industrial locations ranged from 12.4 μg g^{-1} ($\pm$SE 0.5) in Al-Seba to 42.9 μg g^{-1} ($\pm$SE 5.7) in Al-Rumella (**Table 2**).
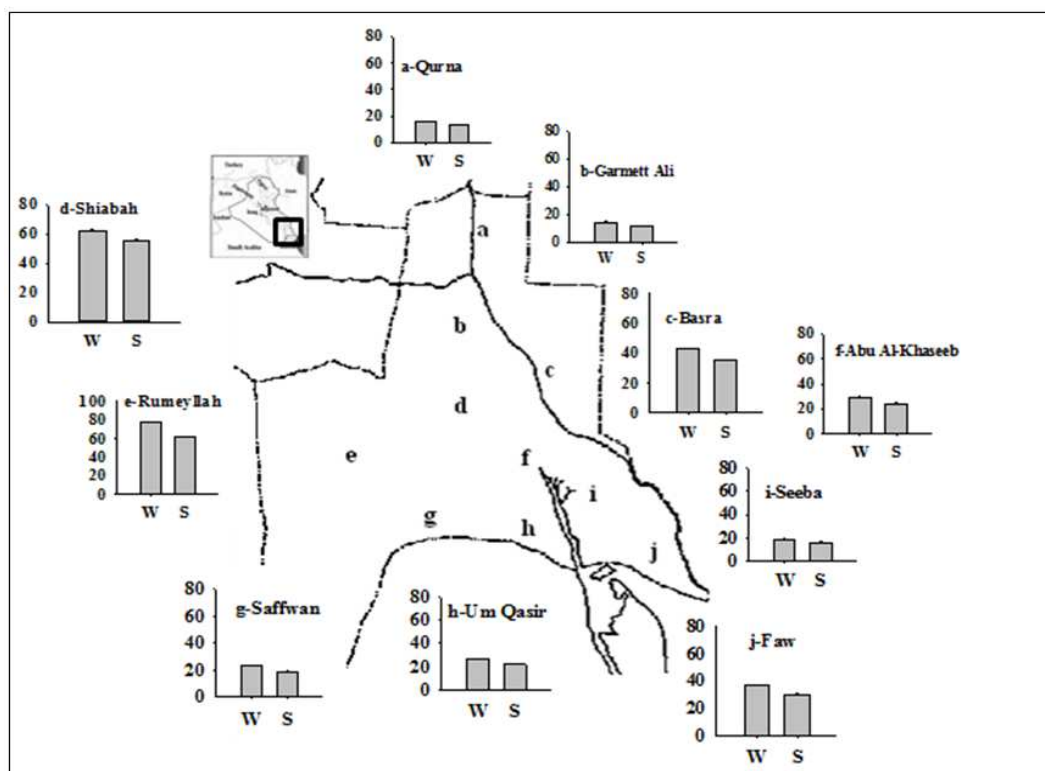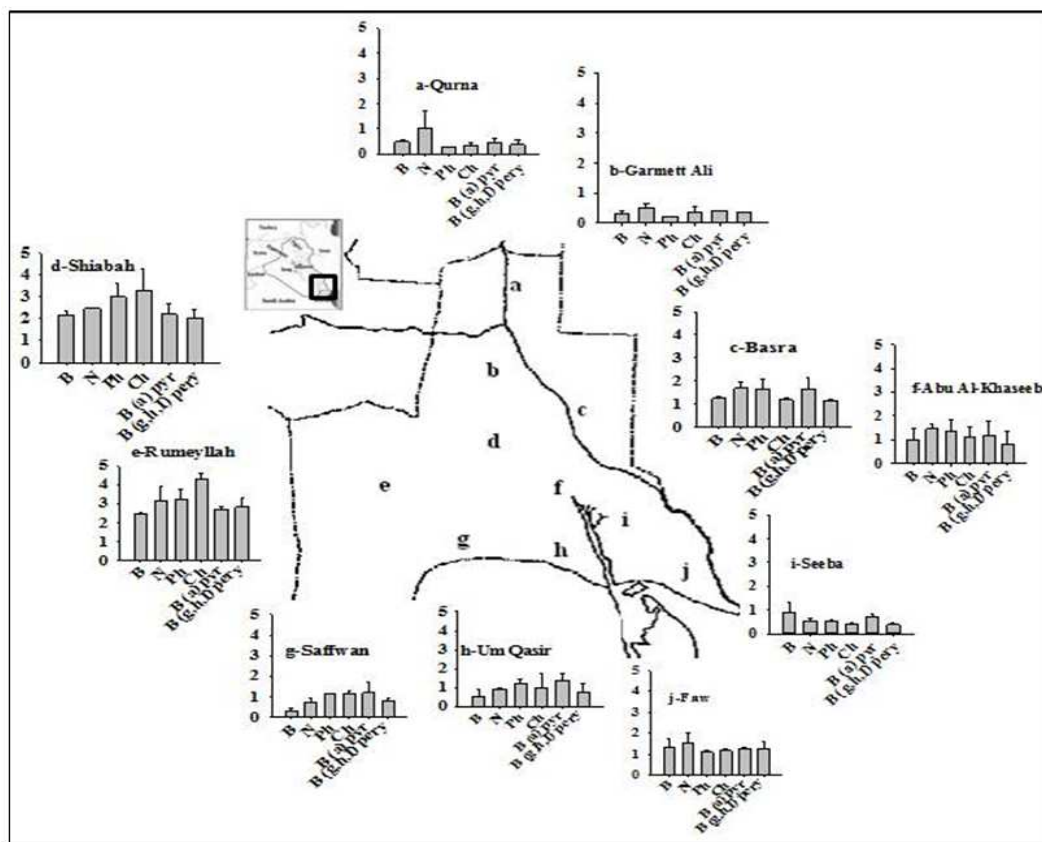
Fig. 1. Average concentrations of total hydrocarbons (µg/g ±SD) at the selected station in Basra governorate during winter and summer 2009

Table 1. Total hydrocarbons concentrations (µg/g ±SD, W = Winter, S = Summer) and poly-nuclear aromatic hydrocarbons (ng/g ±SD) among the sampling locations in Basra city during winter and summer 2009

	Total Hydrocarbons-W	Total Hydrocarbons-S	Benzene	Naphthalene	Phenanthrene	Chrysene	Benzo (a) pyrene	(g,h,I) perylene Benzo
Al-Qurna	15.7(±0.5)	12.9 (±0.3)	0.5 (±0.1)	1.0 (±0.7)	0.3 (±0.0)	0.3 (±0.1)	0.5 (±0.2)	0.4 (±0.2)
Garmat Ali	14.2(±0.5)	11.7 (±0.5)	0.3 (±0.5)	0.5 (±0.5)	0.2 (±0.5)	0.4 (±0.5)	0.4 (±0.5)	0.4 (±0.5)
Center of Basrah	42.6 (±0.3)	35.0 (±0.2)	1.3 (±0.1)	1.7 (±0.3)	1.7 (±0.4)	1.2 (±0.0)	1.6 (±0.5)	1.2 (±0.0)
Al-Shiabah	62.4 (±0.5)	55.3 (±0.5)	2.2 (±0.2)	2.5 (±0.0)	3.0 (±0.6)	3.3 (±1.0)	2.2 (±0.5)	2.0 (±0.4)
Al-Rumella	77.4 (±0.1)	61.6 (±0.7)	2.5 (±0.1)	3.1 (±0.8)	3.3 (±0.5)	4.3 (±0.3)	2.7 (±0.1)	2.8 (±0.5)
Abu Al-Khasib	29.2 (±0.6)	24.2 (±0.5)	1.0 (±0.4)	1.5 (±0.2)	1.3 (±0.5)	1.1 (±0.4)	1.2 (±0.6)	0.8 (±0.5)
Al-Seeba	18.7 (±0.4)	16.0 (±0.1)	0.9 (±0.4)	0.5 (±0.1)	0.5 (±0.1)	0.4 (±0.1)	07 (±0.2)	0.4 (±0.1)
Saffwan	22.8 (±0.6)	18.8 (±0.4)	0.3 (±0.2)	0.8 (±0.2)	1.1 (±0.0)	1.2 (±0.2)	1.2 (±0.5)	0.8 (±0.2)
Um Qasir	26.2 (±0.1)	21.6 (±0.4)	0.5 (±0.4)	0.9 (±0.1)	1.3 (±0.2)	1.0 (±0.8)	1.4 (±0.4)	0.7 (±0.5)
Al-Fao	37.2 (±0.2)	30.4 (±0.5)	1.4 (±0.4)	1.6 (±0.4)	1.1 (±0.1)	1.2 (±0.1)	1.3 (±0.1)	1.3 (±0.3)

The total average odd-even carbon numbers of n-alkanes, CPI values, Pristane/Phytane ratio, Pristine/C_{17} ratio, Phytane/C_{18} ratio and UCM values in soil of the urban and industrial stations are listed in **Table 3**. In general, the calculated Indies indicate that hydrocarbons sources in the urban stations are mostly biogenic origins which are mainly organic matter originating from land plants (Barakat et al., 2001) or resulted due to microbial activity (Wang and Fingas,

2003), except in Al-Shiabah and Al-Qurna stations, where the hydrocarbons sources were mainly anthropogenic origins. The anthropogenic sources in Al-Qurna station is mainly contributed to the high urban activities, while in Al-Shiabah station can be related to the impact of the oil refiner in Al-Rumella. The high UCM values represented in all soil samples during the study period indicate recent hydrocarbons contamination, which mainly petroleum.

Fig. 2. Average concentrations of polynuclear hydrocarbons (ng/g ±SD; B = benzene, N = naphthalene, Ph = phenanthrene, Ch = chrysene, B (a) pyr = benzo (a) pyrene, B (g,h,i) = benzo (g,h,i) perylene) at the selected station in Basra governorate during winter and summer 2009

Table 2. Mean n-alkanes concentrations (μg/g) and standard error in the soil samples of the selected stations in Basra governorate during the study period

Carbon Chain	Al-Qurna	SE	Garmat ali	SE	Center of basra	SE	Al-Shiabah	SE	Al-Rumella	SE	Abu Al-Khasib	SE	Al-Seba	SE	Saffwan	SE	Um Qasir	SE	Al-Fao	SE
C_{12}	0.31	0.3	0.15	0.1	0.55	0.5	1.77	0.3	2.49	1.0	0.21	0.2	0.20	0.2	0.31	0.3	0.32	0.3	0.36	0.3
C_{13}	0.29	0.2	0.25	0.2	0.48	0.3	1.63	1.0	1.87	0.1	0.46	0.1	0.18	0.2	0.32	0.3	0.61	0.4	0.48	0.7
C_{14}	0.73	0.7	0.31	0.3	0.92	0.2	1.98	0.8	1.47	0.6	0.71	0.3	0.17	0.1	0.63	0.7	0.51	0.3	0.44	0.5
C_{15}	0.35	0.4	0.35	0.2	0.84	0.8	1.43	0.9	2.32	0.3	0.26	0.1	0.21	0.1	0.36	0.2	0.62	0.4	0.32	0.3
C_{16}	0.38	0.3	0.06	0.0	0.42	0.9	1.89	1.1	1.54	1.5	0.40	0.2	0.38	0.1	0.56	0.3	0.57	0.5	0.40	0.3
C_{17}	0.44	0.3	0.25	0.2	1.59	0.4	1.93	1.5	2.32	1.3	0.98	0.3	0.73	0.2	0.53	0.5	0.64	0.6	0.99	0.3
C_{18}	0.56	0.3	0.24	0.2	1.48	0.6	1.99	1.8	2.81	1.8	0.50	0.1	0.63	0.1	0.62	0.5	0.78	0.7	0.96	0.3
C_{19}	0.57	0.5	0.21	0.4	1.59	1.0	1.93	1.8	2.70	1.8	0.38	0.3	0.58	0.3	0.30	0.6	0.63	0.4	1.28	0.5
C_{20}	0.52	0.5	0.59	0.2	1.78	1.5	1.08	2.4	2.30	2.3	0.57	0.5	0.77	0.4	0.78	0.6	0.85	0.8	0.88	0.5
C_{21}	0.65	0.6	0.56	0.4	1.53	1.9	2.85	2.6	2.26	2.0	1.32	1.6	0.32	1.0	0.54	0.5	0.86	0.8	0.87	0.9
C_{22}	0.45	0.5	0.70	0.4	1.54	1.4	1.61	2.6	2.32	1.3	0.66	0.6	0.35	0.7	0.72	0.7	1.55	1.0	1.38	1.2
C_{23}	0.88	0.7	0.91	0.7	1.63	1.0	1.85	1.6	2.30	2.1	1.38	1.3	0.63	0.8	0.89	0.9	0.96	0.9	1.06	1.1
C_{24}	0.78	0.7	0.84	0.5	2.06	1.3	2.96	2.1	2.74	2.3	0.40	0.4	1.24	0.5	0.93	0.9	0.58	0.9	1.22	1.2
C_{25}	0.54	0.5	0.73	0.6	1.63	1.5	1.80	1.6	2.68	2.1	0.45	1.4	0.56	0.4	0.88	0.8	0.86	0.8	1.46	1.0
C_{26}	0.63	0.7	0.56	0.5	1.92	1.9	1.92	1.9	2.86	1.1	1.36	1.0	1.64	0.9	0.69	0.6	1.63	0.6	1.91	1.8
C_{27}	0.33	0.2	0.63	0.6	1.58	1.8	1.80	1.6	2.77	2.5	0.34	0.4	1.20	0.5	0.65	0.6	0.77	0.8	1.02	0.7
C_{28}	0.39	0.3	0.67	0.5	1.52	1.6	1.98	1.9	2.68	2.4	1.21	0.4	1.10	1.6	0.49	0.5	0.53	0.9	1.33	1.3
C_{29}	0.34	0.3	0.42	0.3	1.78	1.6	1.69	1.7	2.57	2.4	0.35	1.2	1.09	0.8	0.94	0.7	0.63	0.8	1.16	1.7
C_{30}	0.29	0.3	0.50	0.5	1.89	1.6	1.86	1.5	1.22	1.9	1.18	0.5	0.32	1.0	0.91	0.7	0.93	0.9	1.15	1.6
C_{31}	0.22	0.2	0.67	0.6	1.43	1.7	1.63	1.8	1.31	2.3	0.15	0.4	0.16	1.6	0.88	0.4	0.84	0.7	0.49	1.6
C_{32}	0.19	0.2	0.59	0.3	0.48	0.9	1.46	1.9	1.12	1.8	0.10	0.1	0.16	0.3	0.65	0.3	0.64	0.5	0.53	0.7
C_{33}	0.12	0.1	0.15	0.1	0.28	0.2	0.46	0.6	0.16	1.1	0.08	0.1	0.10	0.2	0.15	0.2	0.20	0.2	0.23	0.2
C_{34}	0.11	0.1	0.09	0.1	0.25	0.2	0.34	0.3	1.10	1.1	0.11	0.1	0.08	0.0	0.18	0.1	0.16	0.2	0.16	0.1
C_{35}	0.11	0.1	0.08	0.1	0.19	0.2	0.27	0.3	0.79	0.2	0.11	0.1	0.09	0.0	0.16	0.1	0.19	0.2	0.12	0.2
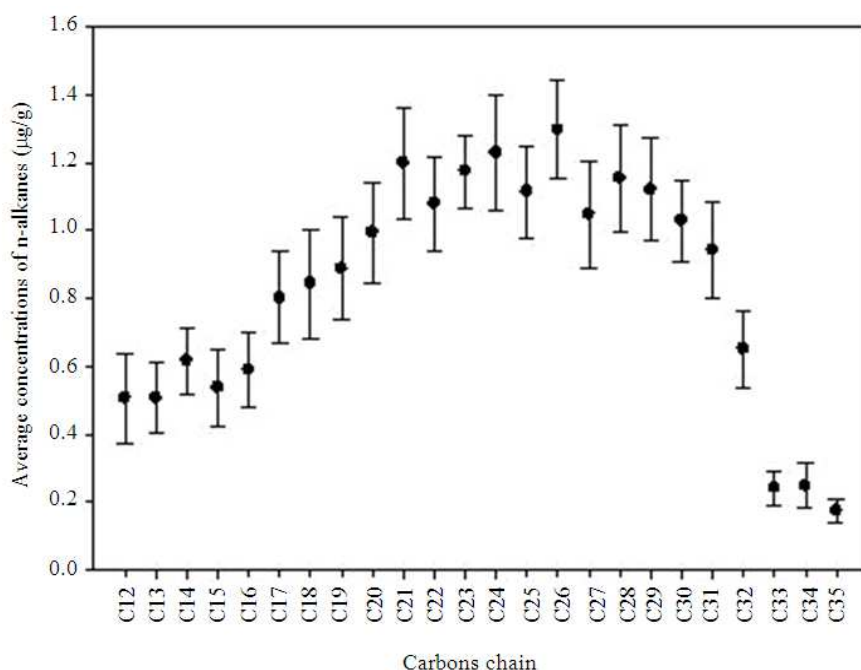
Fig. 3. Chromatographic distributions of carbon chain lengths of the average n-alkanes concentrations ($\mu g/g$ $\pm$SE) from the sampled locations in Basra governorate during winter and summer 2009

Table 3. Odd/Even n-alkanes values, CPI values, Pristane/Phytane ratio, Pristane/C_{17} ratio, Phytane/C_{18} ratio and UCM values in the soil samples of the selected stations in Basra governorate during the study period

	Al-Qurna		Garmat ali		Center of		Al-Rumella		Al-Shiabah		Abu Al-Khasib		Al-Seba		Saffwan		Um Qasir		Al-Fao	
	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S
Odd/Even n-alkane	0.9	0.9	1.0	1.2	1.0	1.0	0.9	0.9	1.0	0.9	0.8	1.7	1.0	1.0	0.9	1.0	0.9	0.9	0.9	0.9
CPI	0.9	0.9	1.0	1.2	1.0	1.0	0.9	0.9	1.0	0.9	1.9	1.7	1.0	1.1	0.9	1.0	0.9	0.9	0.9	0.9
Pristane/Phytane	0.9	0.9	1.1	1.2	1.0	0.9	0.9	0.9	0.9	0.9	2	1.8	1.3	1.5	0.9	1.0	0.9	0.9	0.9	0.9
Pristane/C_{17}	1.0	1.5	0.8	0.9	1.1	1.0	1.2	1.1	1.0	1.0	1	0.9	0.8	0.8	1.1	1.3	1.1	1.3	1.2	1.1
Phytane/C_{18}	1.1	1.1	0.9	0.9	1.0	1.3	1.2	1.2	1.1	1.2	1	0.8	0.9	0.8	1.1	1.1	1.2	1.4	1.0	1.1
UCM	7.0	5.8	3.3	2.1	9.0	7.6	9.5	7.5	11.4	9.5	2.5	2.4	3.2	3.0	7.0	6.9	8.3	7.3	8.5	7.0

4. CONCLUSION

The survey determined the background information of total hydrocarbons concentrations in the soil and their distribution in the industrial zone and their surrounded urbanization in Basra Governorate. The present data may be used in future environmental impact assessment studies. The refined oils and gas production plants, electrical generating stations, oil wastes discharges, transportation and domestic activities could be the possible sources of anthropogenic hydrocarbons in the sampled locations. Similar findings were reported by several authors for example (Li *et al.*, 2006; 2010;

Mielke *et al.*, 2001). On the other hand seeps from oil deposits, degradation of organic matter and synthesis by certain organisms might represent the natural sources Meharg *et al.* (1998). Part of the urban locations areas are subject to contaminated by petroleum hydrocarbons (Sojinu *et al.*, 2010). Every possible effort should be made to minimize petroleum plants wastes by applying outfall licenses to specify permissible levels on the basis of the most toxic fractions of petroleum released into the environment. In addition, aromatic hydrocarbons should be carefully monitored in the soil in order to provide their minimum and acceptable levels within the industrial and urbanization areas to human, fauna and flora.

5. ACKNOWLEDGEMENT

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