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n-Alkanes in surficial soils of Basrah city, Southern Iraq

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Abstract A study has been carried out to determine the distribution of aliphatic hydrocarbons in surface soils of Basrah city, southern Iraq. One hundred twenty eight surface soil samples (0-10 cm depth) were collected from sixteen sites around Basrah city covering commercial ports, industrial and oil operational locations, urban and rural areas. Hydrocarbons were extracted with mixture of benzene: methanol using soxhlet technique and fractioned with silica-alumina column. Characterization of individual hydrocarbon components was carried out using gas chromatography-flame ionization detector. Average of the total identified *n*-alkanes concentrations in soil samples were found ranging from 03.575 to 21.266 μg g^{-1} dry weight. Carbon Preference Index (CPI) values for *n*-alkanes varied between 0.893 and 5.57. The isoprenoids, pristane and phytane were detected in most soil samples. Unresolved Complex Mixture (UCM) values ranged from 5.2 to 12.3 μg g^{-1} dry weight. No significant correlation between soil , % Total Organic Carbon (% TOC) and the concentrations of *n*-alkanes was observed. Results indicated that the aliphatic hydrocarbons were from both biogenic and anthropogenic sources. Generally, the results show that the total *n*-alkanes concentrations were higher in winter and autumn than that recorded for spring and summer.

Keywords Soil pollution; *n*-alkanes; Gas Chromatography; Basrah city

Introduction

Soil contamination by hydrocarbons is an important problem in many areas of the oil-producing countries. Hydrocarbons can contaminate soil through many sources that include leakage of storage tanks and pipelines, land disposal of petroleum wastes and accidental spills (Barakat et al., 2001; Kèdomè et al., 2012). Although most of the hydrocarbons present in the soil resulting from anthropogenic activities. Soil contains relatively small amounts of natural hydrocarbons (biogenic) such as those synthesized by certain organisms (e.g. higher plants and microorganisms) (Zhang et al., 2012). The hydrocarbons in soil are strongly related to the sorbet organic matter and this depended on the nature of the hydrocarbon and the organic matter content (Sadler and Connell, 2003). However, the hydrocarbons can be removed from the soil by different processes such as volatilization, reaction, leaching and biodegradation. Some of these processes take a long time to remove hydrocarbons from the soil depending on the environmental conditions, so the part of these compounds will remain steady in the soil and become more resistant (Kèdomè et al., 2012; Olubunmi et al., 2012). The increase in the concentrations of hydrocarbons in the soil may cause adverse effects on the ecosystem, and some hydrocarbons are considered carcinogenic and mutagenic where they can cause serious health problems for humans and other living resources (Iturbe et al., 2004; Teaf et al., 2008).

Basrah, a city located in southern Iraq be rich in oil. Many oil operations had achieved in this city after 2003 by many international oil companies, So high concentrations of hydrocarbons expects their presence in its soil. In addition to the oil operations there are other sources of petroleum hydrocarbons may also contaminate the soil of this region include industrial factories, electric power stations and gas production plants. However, there are few studies estimated the levels of petroleum hydrocarbons in this city (Douabul et al., 2012), which must have precedence from the environmental point of view. Thus, the present study was carried out to determine the distribution and seasonal variations of petroleum hydrocarbons in sixteen sites in Basrah governorate. The results obtained in this study can service as baseline for future environmental impact assessment of oil operations.

Material and Methods

Four types of sampling sites were selected across Basrah city for soils collection. The first type of sites are commercial ports (Al-Fao and Um-Qasir) and their soils were heavily influenced by oil exportation. The second type is industrial and/or oil operational locations including: Al-Shiabah, Al-Rumella, Kor-Al-Zubair, and Al-burjsia. These sites are specific to anthropogenic activities. The third type of sites is urban areas including: Center of Basrah, Saffwan, Al-Zubair and Al-Tanoma. The soils of these areas are generally subject to a variety of activities in a different degrees such as traffic, houses and workshops (mechanics, carpentry etc), sale of goods of all kinds and petroleum products handling facilities. The last type of sites is rural areas (Garmat Ali, Al-Seeba, Al-Daer, Ras-Al-Bisha and Abu Al-Khasib) and their soils considered low contaminated and are sometimes covered with vegetation.

A total of one hundred twenty eight (128) surface soil samples (0-10 cm depth) were collected using hand auger from the above stations during 2015 to account for winter, spring, summer, and autumn seasons. The locations in Basrah city for the collection of soils are shown in Figure (1) and were geo-located with Global Positioning System (GPS) to ensure consistency as given in Table (1).

Soil 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. The Total Organic Carbon (TOC) in soil samples were analysed using Walkey's and Black titration method, in which the organic carbon is oxidized by dichromate ions, and the quantity of excess dichromate ions is then back titrated with ferrous ion.

The method used to extract, fractionate, and analyzed the hydrocarbons from the soil was based upon that of Jeng and Huh (2006) and Tuteja et al., (2011) with some modification as indicated. A 25 g amount of freeze-dried soil was placed in soxhlet apparatus and extracted with 150 ml benzene: methanol mixture (3:1) for 8 hours. The extract was storage and the soil was further extracted with fresh solvents. The combined

Figure 1 Study areas and sampling locations in the Basrah city

Table 1 Soil sampling sites in Basrah city

Stations	Location	
Garmat Ali	30 °48'10.6" N	47 °45'03.8" E
Saffwan	30 °07'10.1" N	47 °39'44.9" E
Al-Qurna	31 °00'24.6" N	47 °26'25.6" E
Ras-Al-Bisha	29 °56'33.8" N	48 °34'37.4" E
Al-Seeba	30 °20'16.5" N	48 °15'34.5" E
Al-Tanoma	30 °30'46.0" N	47 °51'14.4" E
Abu Al-Khasib	30 °27'44.5" N	48 °00'06.0" E
Al-Daer	30 °48'10.6" N	47 °34'49.8" E
Al-Zubair	30 °29'48.1" N	47 °44'06.6" E
Al-Shiabah	30 °27'16.0"N	47 °39'43.0" E
Al-Fao	29 °58'28.6" N	48 °29'09.5" E
Kor-Al-Zubair	30 °16'45.6" N	47 °44'39.4" E
Center of Basrah	30 °33'00.0"N	47 °47'10.0"E
Al-burjsia	30 °23'32.3" N	47 °35'45.2" E
Al-Rumella	30 °34'08.0"N	47 °21'09.0"E
Um Qasir	30 °05'23.7" N	47 °56'38.5" E

extract was then reduced in volume to 10 ml by a rotary vacuum evaporator and was sabonified for 2 hours with a solution of 4N KOH in 1:1 benzene: methanol. Then the extract was dried by anhydrous Na_2SO_4 and concentrated by a stream of nitrogen. The concentrated extract was separated into two fractions by column chromatography. The column contained 8g of 5 % deactivated alumina (100-200 mesh) on the top and silica (100-200 mesh) in the bottom which were previously extracted with methylene chloride for 36 hours, dried at 130 ℃ for 24 hours, and deactivated with deionized water. The extract was applied to the head of column. The first fraction containing the aliphatic hydrocarbons was eluted from column with *n*-hexane and the second with benzene. The second fraction saved for further analysis and the composition of only the first fraction will be discussed. After most of the solvent was removed from the *n*-hexane fraction, the sample was then analyzed in a Allegent capillary gas chromatography (GC) in which the helium gas was used as a carrier gas with a linear velocity of 1.5 ml minutes^{-1}. The operating temperatures for detector and injector were 350 ℃ and 320 ℃, respectively. The silica capillary column was operated under initial, final and rate temperatures that programmed as follows: Initial temperature was 60 ℃ for 4 min while final temperature was 280 ℃ for 30 min and rate was 4 ℃/ minutes.

Quantification of peaks and identification of hydrocarbons were done by computing integrator. 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 (Askari and Pollard, 2005; Zrafi et al., 2013). Pristane/Phytane ratio and the Unresolved Complex Mixture index (UCM) were used as indicators of petroleum contamination (Tolosa et al., 2005; Wang et al., 2011) and to estimate the degree of bacterial degradation (Punyu et al., 2013).

For quality assurance, the laboratory blank and spiked matrix (internal standard spiked into soil) was analyzed. Results showed that there were no significant background interferences. Recovery assays for standards aliphatic compounds ranged from 85% to 91%. Standard deviation for the method was less than 10 % based on replicate analysis. All concentrations were expressed on a soil dry weight basis.

Results and Discussion

The average concentrations of total *n*-alkanes in soils of Basrah city and the *n*-alkanes calculated indies are listed in Table (2, 3, 4 and 5). The concentrations ranged between 3.575 and 21.266 µg g^{-1} dry weight, with an overall average of 9.152 µg g^{-1} dry weight. Insufficient documentation exists for total *n*-alkanes content in Basrah city soils. Results obtained from the present study show that samples taken from the soils of stations Ras-Al-Bisha, Al-Qurna, Al-Seeba, Garmat Ali, Abu Al-Khasib, Saffwan, Al-Daer, Al-Tanoma, and Al-Zubair displayed relatively low values of total *n*-alkanes, ranging from 3.575 to 5.467 µg g^{-1} dry weight. These low total *n*-alkanes concentrations may be regarded as the natural background levels in these areas. Relatively high concentrations of total

hydrocarbons (10.88 to 21.266 µg g^{-1} dry weight) were found in those soils collected from stations of Al-Rumella, Al-Shiabah, Al-burjsia, Kor-Al-Zubairand, Center of Basrah, Al-Fao, and Um-Qasir which associated with discharges of petroleum wastes. For example, sampling stations Al-Rumella, Al-Shiabah, Al-burjsia, and Kor-Al-Zubair hosted the largest oil refineries, gas production plant and petrochemical factory as well as these stations represented the sites of crude oil extraction and production (oilfields). Station Center of Basrah received petroleum wastes from houses and workshops activities, gasoline stations, transportation and industries activities, electrical generating plants and units, leakages from tanks or tanker trucks and dump of waste petroleum by-products on soils. Al-Fao and Um-Qasir ports are stations suspected to be influenced by oil exportation. Figure (2) shows the spatial concentrations profiles of total *n*-alkanes among different sampling stations.

The concentrations of total *n*-alkanes in soils from 16 sites varied from season to season (Table 5 and Figure 3), showing a decreasing order of winter (average= 12.587 µg g^{-1}) > autumn (average= 10.054 µg g^{-1}) > spring (average= 7.416 µg g^{-1}) > summer (average= 6.552 µg g^{-1}), with the winter season being the highest. Williams et al., (2006) reported that temperature represents one of the most important factors limited the rates of hydrocarbons microbial degradation in the winter. It is possible that the weather impacted the activities of the microorganisms in the soils, which degrade the hydrocarbons. The high temperature seemed to offer the best environmental conditions to support the highest rates of hydrocarbons biodegradation. During the warmer months, hydrocarbons biodegradation is rapid while during the colder month the biodegradation process is less efficient. Hence, biodegradation was

Table 2 Average of *n*-alkanes concentrations (μg g^{-1}) and standard error of the soil of Basrah city during the study period

Carbon chain	Garmat Ali	ES	Safwan	ES	Al-Qurna	ES	Ras-Al Bisha	ES	Al-Seeba	ES	Al-Tanoma	ES	Abu Al-Khasib	ES	Al-Daer	ES	Al-Zubair	ES
C_{11}	0.002	1.1	0.010	0.6	0.012	0.7	0.002	0.5	0.052	0.7	0.064	0.6	0.013	0.8	0.067	0.3	0.017	0.5
C_{12}	0.126	0.6	0.050	0.7	0.101	0.5	0.001	0.7	0.052	0.1	0.203	0.5	0.031	0.6	0.195	0.4	0.037	1.2
C_{13}	0.140	0.3	0.040	0.2	0.058	0.8	0.015	0.3	0.052	1.7	0.246	0.3	0.018	0.5	0.188	0.3	0.081	0.4
C_{14}	0.016	0.8	0.011	0.7	0.002	0.2	0.043	0.5	0.072	0.8	0.015	0.8	0.056	0.6	0.048	1.0	0.013	0.3
C_{15}	0.042	0.9	0.032	0.4	0.032	0.1	0.052	0.9	0.024	1.2	0.002	0.7	0.010	0.7	0.014	1.1	0.061	0.5
C_{16}	0.051	0.3	0.032	0.9	0.036	0.1	0.113	1.0	0.055	0.7	0.030	0.3	0.116	0.8	0.005	1.3	0.022	0.6
C_{17}	0.020	0.3	0.130	0.5	0.015	0.3	0.057	1.3	0.120	0.7	0.141	1.4	0.064	0.3	0.002	1.4	0.100	0.6
C_{18}	0.010	1.3	0.052	1.1	0.066	0.5	0.023	1.4	0.040	0.1	0.050	1.9	0.032	0.2	0.001	0.5	0.040	0.3
C_{19}	0.112	1.5	0.102	1.0	0.146	0.5	0.031	0.5	0.122	0.1	0.057	1.0	0.105	1.1	0.031	0.9	0.152	0.9
C_{20}	0.011	1.0	0.140	1.0	0.238	0.7	0.012	1.5	0.069	1.7	0.022	1.8	0.239	0.2	0.082	0.8	0.129	0.6
C_{21}	0.221	0.8	0.100	0.5	0.148	0.8	0.021	0.5	0.126	0.2	0.202	0.7	0.011	1.5	0.072	0.4	0.011	0.1
C_{22}	0.041	0.9	0.180	0.8	0.002	1.2	0.054	1.3	0.047	0.1	0.022	1.7	0.015	1.0	0.102	0.3	0.042	0.1
C_{23}	0.045	0.4	0.101	0.9	0.120	1.1	0.027	0.4	0.062	0.2	0.535	1.4	0.414	0.4	0.352	0.4	0.241	1.0
C_{24}	0.213	0.2	0.105	0.3	0.003	1.5	0.113	0.3	0.051	0.9	0.039	0.3	0.067	1.8	0.053	0.5	0.082	0.6
C_{25}	0.180	0.5	0.485	0.3	0.655	0.7	0.325	0.5	0.420	1.0	0.458	0.7	0.806	0.6	0.570	0.1	0.820	0.7
C_{26}	0.240	0.8	0.071	0.2	0.071	1.8	0.135	0.6	0.058	0.9	0.120	0.2	0.067	0.8	0.110	0.7	0.100	0.9
C_{27}	0.721	0.7	0.735	0.7	0.448	0.4	0.771	0.6	0.421	0.3	0.661	0.1	0.696	0.3	0.671	1.0	0.632	0.3
C_{28}	0.035	0.2	0.021	0.5	0.042	0.6	0.013	0.7	0.037	0.3	0.101	1.2	0.020	0.4	0.002	1.4	0.064	0.2
C_{29}	0.631	1.4	0.761	1.5	0.457	0.1	0.532	0.6	0.747	0.2	0.582	0.4	0.729	0.9	0.822	1.1	0.648	0.4
C_{30}	0.112	1.3	0.026	1.8	0.021	0.1	0.043	0.2	0.061	0.5	0.102	0.4	0.030	0.6	0.031	1.5	0.034	0.4
C_{31}	0.801	0.5	0.568	0.4	0.515	0.5	0.481	0.3	0.828	0.6	0.710	0.8	0.552	0.3	0.741	1.9	0.932	1.5
C_{32}	0.043	0.6	0.151	0.3	0.012	0.7	0.033	0.1	0.051	0.1	0.001	0.3	0.040	0.1	0.132	0.4	0.241	1.5
C_{33}	0.506	0.7	0.727	0.6	0.714	0.3	0.531	0.1	0.568	1.1	0.916	0.3	0.422	0.1	0.530	0.2	0.833	1.4
Total	4.386		4.757		5.467		4.182		5.421		4.942		3.916		3.575		4.594	

Table 3 Average of odd and even *n*-alkanes, CPI, UCM, pristane and phytane, and pristane/phytane ratio values of the soil of Basrah city during the study period

n-alkane indies	Garmat Ali	Saffwan	Al-Qurn a	Ras-Al Bisha	Al-Seeba	Al-Tano ma	Abu Al-Khasib	Al-Daer	Al-Zubai r
Total ood	3.421	3.791	4.528	3.542	4.574	4.060	3.320	2.845	3.840
Total even	0.965	0.966	0.939	0.640	0.847	0.882	0.596	0.730	0.754
CPI	3.545	3.928	4.822	5.534	4.793	4.603	5.570	3.897	5.092
UCM (μg g^{-1})	6.800	6.500	7.400	5.200	7.700	7.900	5.900	5.300	7.100
Pristane (μg g^{-1})	0.524	0.439	0.555	0.387	0.439	0.479	0.293	0.398	0.484
Phytane (μg g^{-1})	0.561	0.431	0.582	0.400	0.437	0.448	0.311	0.359	0.532
Pristane/Phytane	0.934	1.018	0.953	0.967	1.004	1.069	0.942	1.100	0.909

Table 4 Average of *n*-alkanes concentrations (μg g^{-1}) and standard error of the soil of Basrah city during the study period

Carbon chain	Al-Shia bah	ES	Al-Faw	ES	Kor-Al -Zubair	ES	Center of Basrah	ES	Al-burj sia	ES	Al-Ru mella	ES	Um-Qasir	ES
C_{11}	0.731	0.6	0.479	1.4	0.421	0.4	0.441	1.3	0.631	0.1	0.893	1.7	0.432	0.5
C_{12}	0.241	0.4	0.125	0.3	0.158	0.8	0.122	1.6	0.242	0.3	0.318	0.3	0.113	0.4
C_{13}	0.650	1.5	0.532	0.5	0.654	0.9	0.502	0.5	0.535	0.4	0.792	0.4	0.342	0.6
C_{14}	1.370	0.3	0.880	0.5	0.962	0.2	0.928	0.7	1.340	0.2	1.488	0.5	0.815	0.7
C_{15}	0.894	1.2	0.482	0.8	0.524	1.0	0.427	0.3	0.601	0.4	0.866	0.4	0.551	0.7
C_{16}	1.562	0.7	0.947	0.2	0.932	1.3	0.875	0.5	1.141	0.3	1.610	0.2	0.816	0.2
C_{17}	0.723	0.5	0.590	0.4	0.337	1.8	0.510	0.8	0.626	0.5	0.741	0.5	0.421	1.5
C_{18}	1.382	0.9	0.873	0.9	0.967	0.7	0.961	0.9	1.472	1.3	1.516	0.1	0.821	1.7
C_{19}	0.703	0.9	0.493	1.0	0.552	0.6	0.410	0.1	0.722	1.5	0.885	0.1	0.364	1.0
C_{20}	1.232	1.0	0.861	1.3	0.882	0.4	0.861	0.2	1.313	1.3	1.572	0.6	0.852	0.4
C_{21}	0.741	0.1	0.542	1.7	0.565	0.2	0.415	0.5	0.625	0.6	0.843	0.4	0.345	0.3
C_{22}	1.435	0.1	0.911	1.7	0.998	0.1	0.829	1.4	1.072	0.6	1.636	1.3	0.862	0.6
C_{23}	0.893	0.3	0.580	0.4	0.598	0.3	0.552	1.4	0.717	0.4	0.840	1.0	0.320	0.8
C_{24}	1.690	0.2	0.851	0.8	0.924	0.2	0.884	1.4	1.251	0.8	1.513	0.5	0.820	0.5
C_{25}	0.882	1.0	0.460	0.1	0.540	1.5	0.430	0.5	0.721	0.5	0.899	0.7	0.576	0.9
C_{26}	0.237	0.6	0.148	0.1	0.176	1.6	0.115	0.5	0.111	0.3	0.362	0.8	0.159	1.0
C_{27}	0.812	0.5	0.561	0.1	0.631	0.6	0.421	0.7	0.725	0.2	0.868	0.9	0.462	0.1
C_{28}	0.234	0.6	0.171	0.2	0.112	0.4	0.139	0.9	0.229	0.1	0.241	0.9	0.124	0.3
C_{29}	0.782	0.8	0.442	0.6	0.513	0.2	0.564	0.7	0.622	1.0	0.852	0.4	0.412	0.3
C_{30}	0.246	0.5	0.213	0.8	0.143	0.3	0.182	0.8	0.202	1.3	0.373	0.6	0.196	0.5
C_{31}	0.615	0.3	0.498	0.4	0.661	0.5	0.421	0.3	0.523	0.4	0.761	0.5	0.442	1.5
C_{32}	0.179	0.2	0.133	0.6	0.132	1.6	0.131	0.2	0.101	0.5	0.352	0.3	0.081	1.7
C_{33}	0.730	0.1	0.595	0.7	0.541	0.1	0.524	0.4	0.767	0.6	0.793	0.2	0.522	0.3
C_{34}	0.253	1.6	0.141	0.7	0.153	0.7	0.162	0.3	0.161	1.4	0.252	0.5	0.032	0.1
Total	19.217		12.508		13.076		11.806		16.45		21.266		10.88	

Table 5 Average of odd and even *n*-alkanes, CPI, UCM, pristane and phytane, and pristane/phytane ratio values of the soil of Basrah city during the study period

n-alkanes indies	Al-Shiabah	Al-Faw	Kor-Al-Zubair	Center of Basrah	Al-burjsia	Al-Rumella	Um- Qasir
Total ood	9.156	6.254	6.537	5.617	7.815	10.033	5.189
Total even	10.061	6.254	6.539	6.189	8.635	11.233	5.691
CPI	0.910	1.000	0.990	0.907	0.905	0.893	0.986
UCM (μg g^{-1})	12.300	9.000	8.800	9.500	11.800	10.300	8.600
Pristane (μg g^{-1})	0.635	0.612	0.764	0.782	0.652	0.961	0.821
Phytane (μg g^{-1})	0.767	0.743	0.782	0.815	0.718	0.961	0.971
Pristane/Phytane	0.867	0.823	0.976	0.959	0.908	1.000	0.845

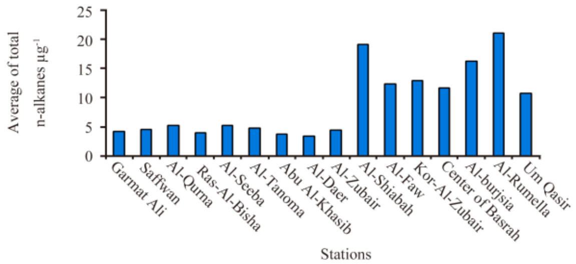

Figure 2 The spatial profiles of the total of *n*-alkanes concentrations average of the Basrah city soil

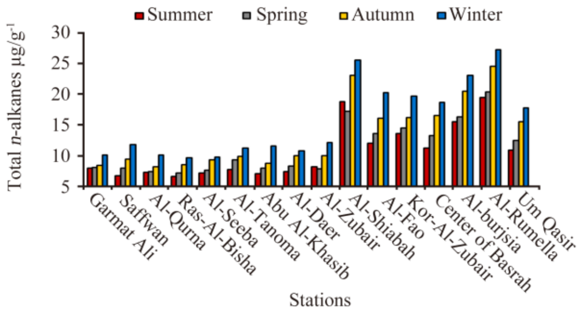

Figure 3 The spatial trend of the total of *n*-alkanes concentrations of the Basrah city soil during different season

Table 6 Total of *n*-alkanes concentrations (μg g^{-1}) of the soil of Basrah city during different season and % TOC values

Stations	Summer	Spring	Autumn	Winter	% TOC
Garmat Ali	3.535	3.689	4.175	6.145	0.85
Saffwan	2.051	3.536	5.363	8.078	0.46
Al-Qurna	2.719	2.959	3.888	6.098	0.81
Ras-Al-Bisha	1.997	2.575	4.208	5.52	0.75
Al-Seeba	2.612	3.182	5.174	5.76	0.70
Al-Tanoma	3.326	5.131	5.796	7.431	0.82
Abu Al-Khasib	2.519	3.594	4.481	7.782	0.84
Al-Daer	2.927	3.949	5.946	6.946	0.76
Al-Zubair	3.885	3.467	5.983	8.533	0.61
Al-Shiabah	16.439	14.547	21.458	24.424	0.53
Al-Fao	8.331	10.308	13.236	18.157	0.73
Kor-Al-Zubair	10.23	11.324	13.31	17.44	0.63
Center of Basrah	7.509	9.806	13.705	16.204	0.64
Al-burjsia	12.481	13.45	18.451	21.418	0.64
Al-Rumella	17.244	18.286	23.189	26.345	0.66
Um Qasir	7.03	8.86	12.51	15.12	0.67
Total	104.835	118.663	160.873	201.401	
Average	6.552	7.416	10.054	12.587	

the most effective in the spring and summer seasons of Basrah city soils.

The gas chromatographic profiles of *n*-alkanes in the soil samples are shown in (Figure 4). The GC traces are dominated by *n*-alkanes extending from C_{11} to C_{34}. *n*-alkanes, representing two distinct sources, are evident on the basis of their distribution pattern in samples collected. For stations Al-Rumella, Al-Shiabah, Al-burjsia, Kor-Al-Zubairand, Center of Basrah, Al-Fao, and Um-Qasir which the most abundant *n*-alkanes are generally C_{14} to C_{24}, while the least abundant are the *n*-alkanes of C_{27}, C_{29} and C_{31}. The dominance of the *n*-alkanes in the range C_{18} to C_{24}, suggests relatively petroleum inputs (Harji et al., 2008; Wang et al., 2011). This has been verified by the presence of a strong UCM in the GC profiles. Such compounds, resistant to biological degradation, have been considered as the environmental indicators of long-term petroleum-related contamination (Jeng and Huh, 2006; Punyu et al., 2013). The CPI is also an index used for determining the sources of *n*-alkanes. These stations presented lower values around 1.0 indicating inputs of *n*-alkanes from petroleum related sources (Ekpo et al., 2012; Zrafi et al., 2013) Figure (5 and 6) show the spatial trend of UCM and CPI in soil of Basrah city. At stations Ras-Al-Bisha, Al-Qurna, Al-Seeba, Garmat Ali, Abu Al-Khasib, Saffwan, Al-Daer, Al-Tanoma, and Al-Zubair the main features in GC profiles are notably different from the above stations. In these stations, the long chain compounds prevailed with the C max at C_{27}, C_{29} and C_{31} and presented an elevated odd to even carbon number preference as reflected in the high CPI values. This pattern is characteristic of higher plant waxes and thus reveals the occurrence of prominent terrestrial inputs to these sampling sites (Harji et al., 2008). However, the *n*-alkanes profile indicates that contribution from plant wax hydrocarbons is over shadowed in samples by *n*-alkanes of petroleum origin. This is obvious by the ratio of pristane to phytane and the presence of high relative abundance of UCM.

The pristane and phytane (isoprenoid compounds) were present in most soil samples. They are common indicators for petroleum contamination. The pristine to phytane ratio varies between oils and is thought to reflect the depositional environment of the original source rocks (Wang et al., 2011). A relative high

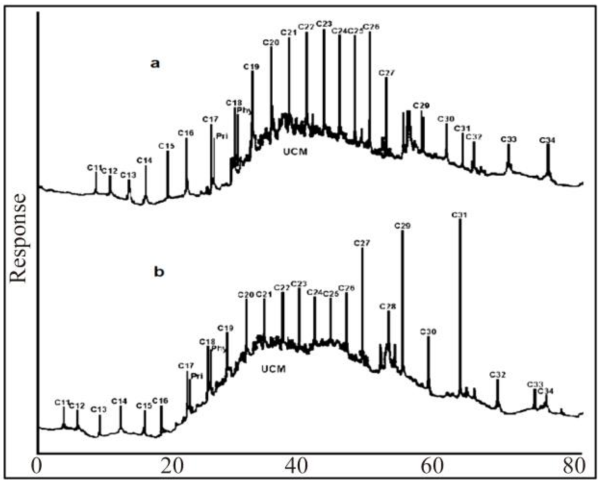

Figure 4 Gas chromatogram of *n*-alkanes from surface soil at stations Center of Basrah (a) and Al-Zubair (b)

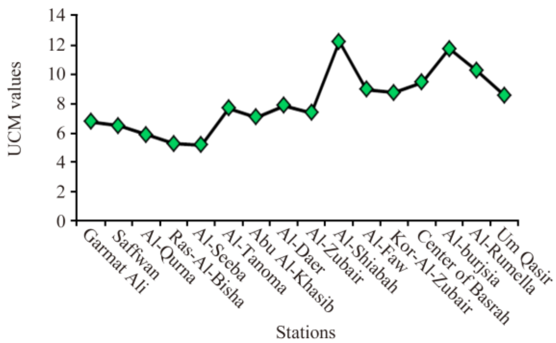

Figure 5 The spatial trend of UCM in surface soil of Basrah city

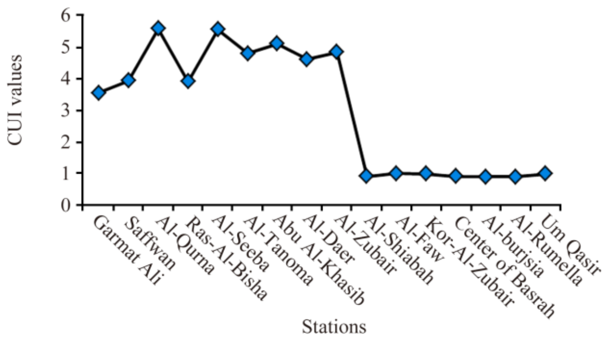

Figure 6 The spatial variation of CPI in surface soil of Basrah city

concentration of pristine alone indicates a biogenic source. In uncontaminated soils, the pristine to phytane ratio is typically between 3 and 5 (Punyu et al., 2013). However, pristane to phytane ratio was low (0.823-1.100) in most of the present samples, indicating mainly petroleum input. The spatial trends of pristane to phytane ratio in soil of Basrah city are shown in Figure (7)

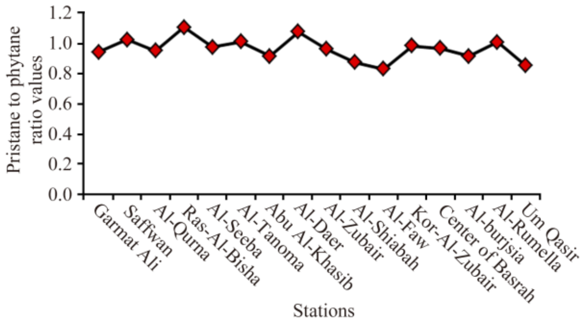

Figure 7 The spatial trend of pristine to phytane ratio in surface soil of Basrah city

The soils of the present study area contained relatively low TOC, with values ranging from 0.61 % to 0.85 %. No significant correlation between % TOC and concentrations of total *n*-alkanes was found (r= 0.189). This suggested that TOC did not play the important role in the distribution of hydrocarbons in the soils of recent area.

Conclusions

The survey determined the background information of aliphatic hydrocarbons concentrations in the soil of Basrah province and their distribution in the industrial area and urban and rural regions surrounding them. The data can be used in the environmental impact assessment in future studies. The concentration of total aliphatic hydrocarbons in soil ranged from 3.575 to 21.266 μg g^{-1} dry weight. Higher concentration of total aliphatic hydrocarbons was accumulate in the city sites which associated with discharges of petroleum wastes (e.g. Al-Rumella, Al-Shiabah, Al-burjsia, Kor-Al-Zubairand, Center of Basrah, Al-Fao, and Um-Qasir). Based on the distribution patterns and diagnostic indices, it can be concluded that the *n*-alkanes in the soil of Basrah city were mainly from both biogenic and anthropogenic sources. Refined oils and gas production plants, power plants, oil wastes discharges, transportation, and domestic activities can be potential sources of hydrocarbons at the sites sampled. Similar results have been reported by several authors for example (Kědomè et al., 2012). On the other hand seeps from oil deposits, degradation of organic matter, and synthesis by certain organisms might represent the natural sources (Zhang et al., 2012). We should make every effort to reduce the waste oil plants through the application of outfall permits to determine the permissible levels on the basis of the most toxic fractions of oil released into the environment. In addition, some hydrocarbons should be carefully monitored in the soil in order to provide minimum acceptable levels within the industrial areas and urbanization to humans, animals and plants.

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