ALIPHATIC HYDROCARBONS IN PETROLEUM-ABUNDANT SOILS IN BASRAH CITY, IRAQ

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Abstract

The sources, allocation and seasonal changes of aliphatic hydrocarbons (AH) has been studied in the soil of Basrah province (southern Iraq). Soil samples were taken from 16- regions representing industrial, civil, rustic and harbors locations. The soil was extracted and the Ah were determined by gas chromatography (GC). The average total soil n-alkanes (Nal) concentrations ranged from 2.916 to 19.259 µg/g dry weight (DW). Branched Nal (pristane (Pri) and phytane (Phy)) were determined in all examined soils. The values of preference index of carbon (PIOC) and un-resolved complex mixture (URCM) varied from 4.716 to 5.033 and 4.400 to 11.300 µg/g DW, respectively. There was no significally relationship between soil total organic carbon (OC) content and Nal concentrations. The Nal in Basrah soil were of either biological or industrial sources. The content of AH was higher in cold seasons (winter (Wi) and autumn (Au)) than in warm seasons (summer (Su) and spring (Sp)).

Keywords: *Soil, Hydrocarbons, Pollution, N-Alkanes, Organic Carbon.*

Introduction

Hydrocarbons (Hy) soil contamination is a trouble for numerous oils producing and importing countries in the world. Sources of Hy in the soil include oil spills from broken transport pipes and damaged storage tanks, disposal of oil waste from production, manufacturing and use sites, and oil spills from various unintended accidents (Zhang *et al.*, 2012; Cocârtă *et al,* 2017). Most of the soil Hy is derived from human activities, however, there are small quantities of bio-Hy in the soil produced from particular organisms such as microbes and plants (Yang *et al.*, 2012). The presence of Hy in the soil is usually associated with organic substances (Al-Saad *et al.*, 2019). Nevertheless, the soil can get rid of Hy by factors such as evaporation, filtration and biological degradation (Truskewycz *et al.*, 2019). Depending on the environmental status, some of these factors may require a long period to eliminate Hy from the soil, and therefore, some of Hy remain stable in the soil (Zhang *et al.*, 2015). The accumulation of Hy in the soil has harmful effects on the living organisms, human and eco-system (Liu *et al.*, 2012; Sari1 *et al.*, 2018).

Basrah province is one of the southern Iraqi cities that are very wealthy in oil. After 2003, many works related to the drilling of oil wells and oil extraction in the city was carried out by several international and national oil companies. Moreover, there are many industries in this city (petrochemicals, fertilizers, iron, steel, food, etc.), and plants for crude oil refining, gas production and electric power generation. In addition to all of the above, Basrah is a densely populated city, with a population of 3 million (Douabul *et al.*, 2012). Therefore, considerable levels of oil contamination are expected in its soil. Nevertheless, a few estimated studies of petroleum Hy have been achieved in this city. Thus, the aim of the current study was to determine the sources and distribution of petroleum Hy and their seasonal changes in several areas of Basrah province.

Materials and Methods

Soil samples were collected from a surface (0 to 15 depths) of 16 different regions of Basrah province using a hand shovel during the WI, AU, SU, and SP seasons of 2022. These regions are Al-Shuaiba (SH), 30°27'16.0" N to 47°39'43.0'' E; Al-Burjussia (BU), 30°23'32.3'' N to 47°35'45.2'' E; Khor-Al-Zubair (KZ), 30°16'45.6'' N to 47°44'39.4'' E; Al-Rumaila (RU), 30°34'08.0" N to 47°21'09.0" E (industrial or oil areas); Al-Tanumah (TA) 30°30'46.0'' N to 47°51'14.4'' E; Al-Basrah (BA), 30°33'00.0" N to 47°47'10.0" E; Al-Zubair (ZU), 30°29'48.1'' N to 47°44'06.6'' E; Safwan (SA), 30°07'10.1'' N to 47°39'44.9'' E (urban areas); Ras-Al-Bisha (RB), 29°56'33.8'' N to 48°34'37.4'' E; Al-Siba (SI), 30°20'16.5'' N to 48°15'34.5'' E; Abu-Al-Khaseeb (AK), 30°27'44.5'' N to 48°00'06.0'' E; Karmat-Ali (KA), 30°48'10.6'' N to 47°45'03.8'' E; Al-Karnah (KR), 31°00'24.6'' N to 47°26'25.6'' E; Al-Dair (DA), 30°48'10.6'' N to 47°34'49.8'' E (rustic areas); Al-Fao (FA), 29°58'28.6'' N to48°29'09.5'' E; and Umm-Qasr (UQ), 30°05'23.7'' N to 47°56'38.5'' E (harbors areas) (Fig. 1).
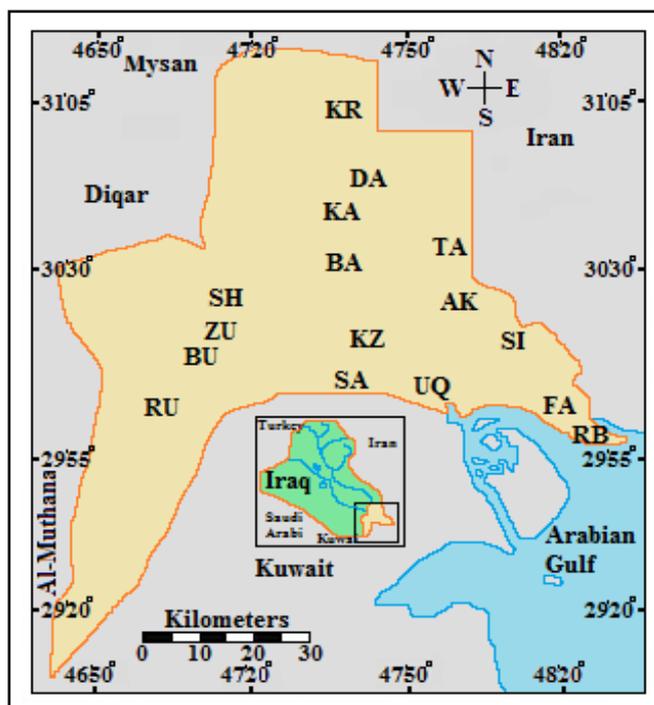
Fig. 1: Basrah province map and sample collection regions.

The samples were transferred to the laboratory and then dried, ground and sifted for analysis. The total OC content was determined by method of Walkey's and Black (1934).

The Hy were extracted from the soil (30 g) with benzene and methanol (3: 1, 250 ml) by Soxhlet for 8 hours following the procedure of Bouzid *et al.* (2011). The extract was reduced (10 ml), sabonified and fractionated into AH and aromatic Hy by column chromatography. The column is filled with silica gel, alumina (10 g), and anhydrous sodium sulfate (1 g) respectively. The n-hexane and benzene (50 ml) were used to obtain AH and aromatic Hy fractions, respectively.

The AH was analyzed by a Ailegent (USA) GC. The working temperatures of detector and injector were 340 °C and 310 °C, respectively. The initial, final and rate operating temperatures of column were 80 °C for 3 min., 260 °C for 28 min. and 4 °C/min., respectively. The blank and spiked matrix into soil was achieved. Recovery of standards aliphatic were 80% to 95%. Standard deviation (SD) of the method was 8% depending on reiterated analysis.

Statistically, the standard error (SE) was achieved between iterations of the Hy concentrations. ANOVA was employed for data analysis and differences in $p < 0.05$ were identified by RLSD. The relationship between some different factors was evaluated by simple correlation with Microsoft Excel. Some Hy indexes were applied to determine the origin of AH. SPSS (version 16) of Windows system (IBM, USA) was utilized to statistically process the data.

Results and Discussion

The average total concentrations of Nal in Basrah province soil varied from 2.916 µg/g DW in the RB region to 19.259 µg/g DW in the RU region (Fig. 2). Fig. 3 represents the average total concentrations of individual Anl in Basrah soil. The current study showed that the soil of the regions of RB, SI, SA, ZU, AK, TA, KA, DA, and KR have comparatively low concentrations of Nal varying from 2.916 µg/g DW (RB) to 4.521 µg/g DW (ZU), which can be considered as a naturalistic background concentrations of these regions. Whereas the regions of FA, UQ, RU, KZ, BU, SH, and BA contain relatively high concentrations of Nal (9.913 µg/g DW (UQ) to 19.259 µg/g DW (RU)), as these concentrations are related with the disposal of petroleum and its products waste in those regions. For example, the regions of RU, KZ, BU and SH receive petroleum waste from oil refineries, gas production plants and petrochemical factories, in addition to being considered areas for petroleum extraction. While the region of BA receives petroleum waste from homes, commercial shops, workshops, transportation, fuel stations, electrical power plants, accidents, unintended oil spills, dumping of waste oil, etc. As for regions of FA and UQ, they are commercial ports affected by oil exports and the movement of commercial and oil vessels.

The concentrations of Nal in Basrah province vary according to seasons. The highest concentrations of Nal were in Wi (4.120 µg/g DW (RB) to 27.000 (RU) µg/g DW), followed by Au (3.195 µg/g DW (RB) to 22 µg/g DW (RU)) and Sp (2.008 µg/g DW (KR) to 16.000 (RU) µg/g DW), and the lowest Nal concentrations were in Su (1.000 µg/g DW (KR) to 12.039 µg/g DW(RU)) (Fig. 4). This may be attributed to the Hy bio-degradation process, which is more effective in warm than cold seasons. It has been found that the rates of microbial degradation of petroleum Hy increase with increasing temperature (Ali, 2019; Zhan *et al.* 2022).

The GC test showed that the Nal prevailing in Basrah province consist of a series of carbon atoms that extend from C_{12} to C_{22}. Depending on the Nal distribution models in the studied samples, there are two identifiable HY sources. The first source is petrogenic in regions of FA, UQ, RU, KZ, BU, SH, and BA which are characterized by the dominance of Nal from C_{18} to C_{24} while Nal C_{27}, C_{29} and C_{31} are the least dominant (Fig. 5). The dominance of Nal with a range of C_{18} to C_{24} indicates comparatively to petroleum inputs at a given site (Wang *et al.*, 2011). This source can also be demonstrated by the presence of severe URCM in GC chromatograms, as these compounds are considered recurrent in microbial degradation and often indicate chronic oil pollution (Adeniji *et al.*, 2017). Possession of the above study regions on values of PIOC approximately 1, also indicates the origins of oil-related Nal (Farid, 2017) (see Table 1).

The second source of Nal is in the regions of RB, SI, SA, ZU, AK, TA, KA, DA, and KR which are described by the predominance of compounds, C_{27} C_{29} and C_{31} in the chain of Nal (Fig. 5), which raised the number of odd carbon atoms versus even, as shown in the PIOC values of these regions. The previous model usually indicates the contribution of terrestrial plant Hy to the above regions (Punyu *et al.*, 2013). Nevertheless, this source is overwhelmed by oil-source Nal, which are evidenced by the Pri to Phy ratio and strong URCM presence for regions (Karem *et al.*, 2017; Zaghden *et al.*, 2017) (see Table 1).

The Pri and Phy were found in all studied soil samples (0.393 and 0.411(AK) to 0.921 (UQ) 0.991 (RU), respectively) and were indications of oil contamination (Frena *et al.*, 2017). The ratio of Pri to Phy varies with different soils, so it is believed that it reflects the sedimentation environment of the original source boulders (Wang *et al.*, 2011). High levels of Pri usually refer bio-Hy (Punyu *et al.*, 2013). The ratio of Pri to Phy for non-polluting soils ranges from 3-5 (Wagener *et al.*, 2008). Nevertheless, in the current samples, this ratio was very low (0.847 (SH) to 1.184 (DA)), suggesting petroleum-inputs (Frena *et al.*, 2017) (see Table 1). Fig. 6 shows the locative tends of Pri/Phy, PIOC and URCM in the Basrah province soil.

The content of total OC in the studied soil ranged from 0.370% (Sa) to 0.810% (Si) (see Table 1). There is no significant correlation between the total OC content and the Nal levels (r = 0.446), indicating that the total OC content does not play a major role in the distribution of HY in Basrah province soil (El Nemr *et al.*, 2007; Al-Saad *et al.*, 2019).
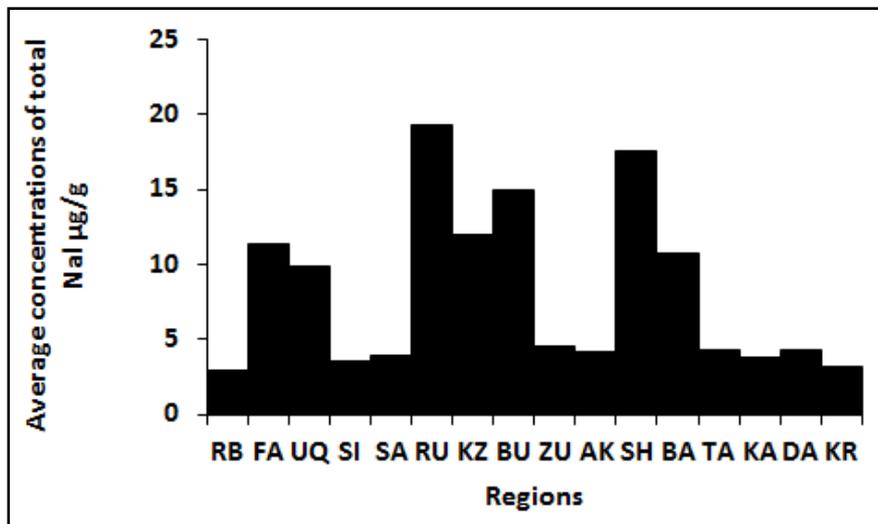
Fig. 2: Locative profiles of average total Nal concentrations in Basrah province soil.
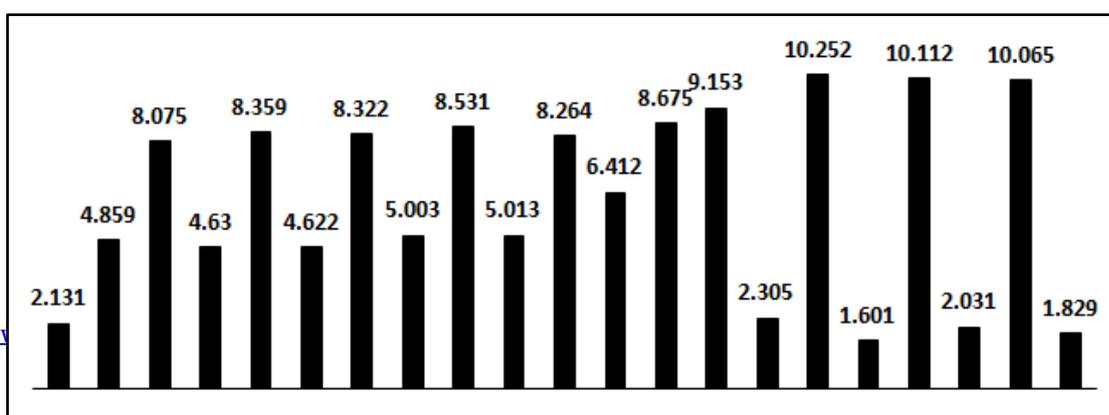
Fig. 3: Average concentrations of total individual NaI of Basrah province soil.
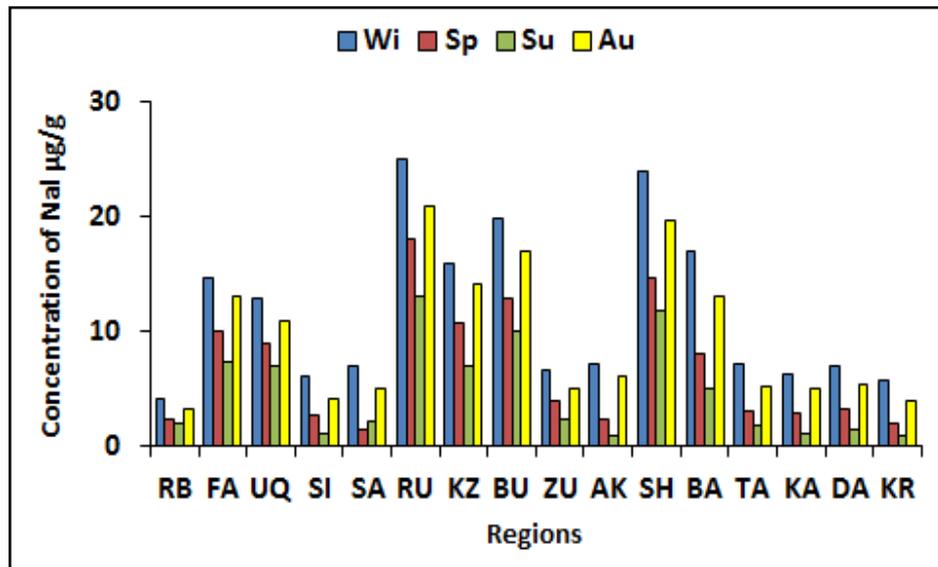
Fig. 4: Locative trends of NaI concentrations in Basrah province soil.
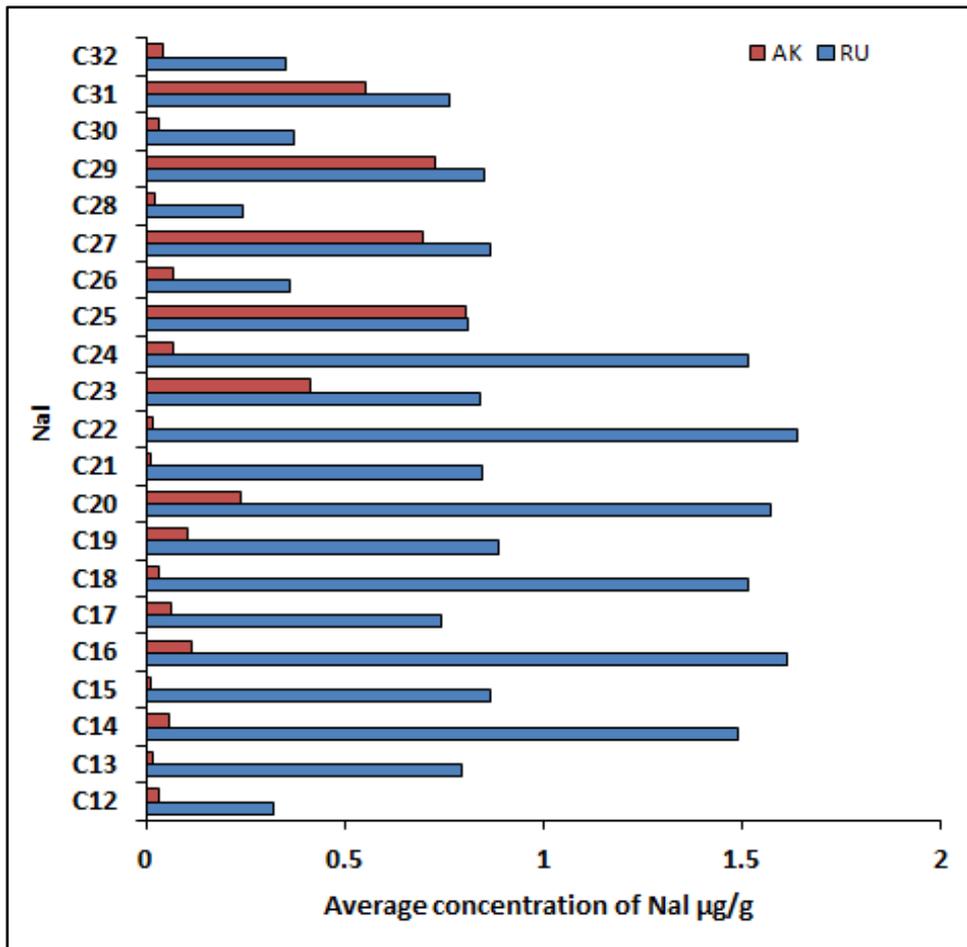
Fig. 5: Nal chromatogram profile in the soils of the AK and RU regions.

Table 1: Nal indices in the soils of Basrah province regions.

Region	Even Nal (Total)	Ood Nal (Total)	Pri (µg/g)	Phy (µg/g)	Pri/Phy	PIOC	URCM (µg/g)	Total OC (%)
RB	0.594	2.322	0.487	0.500	0.974	3.909	4.300	0.660
FA	6.124	5.190	0.712	0.843	0.844	0.847	8.300	0.640
UQ	5.670	4.243	0.921	0.801	1.149	0.748	7.700	0.780
SI	0.604	2.932	0.539	0.537	1.003	4.854	6.100	0.810
SA	0.850	3.073	0.539	0.531	1.015	3.615	5.800	0.370
RU	10.992	8.267	0.861	0.991	0.868	0.752	9.500	0.570
KZ	6.397	5.585	0.864	0.882	0.979	0.873	7.700	0.540
BU	8.485	6.426	0.752	0.818	0.886	0.757	10.400	0.550
ZU	0.824	3.697	0.584	0.632	0.924	4.486	6.200	0.520
AK	0.724	3.415	0.393	0.411	0.956	4.716	4.700	0.750
SH	9.819	7.705	0.735	0.867	0.847	0.784	11.300	0.440
BA	6.038	4.662	0.882	0.915	0.963	0.772	8.600	0.550
TA	0.716	3.604	0.579	0.548	1.056	5.033	6.900	0.730
KA	0.909	2.923	0.624	0.661	0.944	3.215	5.900	0.760
DA	0.772	3.473	0.498	0.459	1.184	4.498	4.400	0.670
KR	0.605	2.604	0.655	0.682	0.960	4.304	6.700	0.720
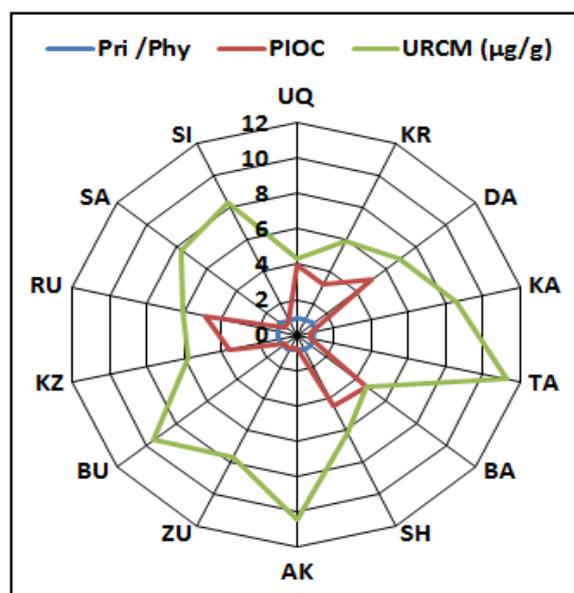
Fig. 6: Locative trends of Pri/Phy, PIOC and URCM in the soils of Basrah province regions.

Conclusions

This study determines background data on AH in Basrah province soil and their allocation in industrial, civil, rustic and harbors regions. Current data can be used to assess futurity ecological damage. Oil refineries, gas production and petrochemical plants, electric power generating units, transportation means, oil waste disposal and various commercial and household events may be potential sources of AH in Basrah soil. Moreover, the bio-Hy created by certain organisms (plants and microorganisms) and bio-degradation of organic substances may constitute the naturalist sources of AH in province soil. Efforts should be made to reduce the petroleum residues in the soil to the permissible limits by applying strict laws and regulations on the basis that most petroleum compounds are polluted for the ecosystem and cause harmful effects on humans and other organisms. as well, some dangerous Hy in the soil must be closely monitored to obtain acceptable levels of them in industrial processes, urban and rural regions.

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