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An Analytical Study on Petroleum Hydrocarbons Contamination in the Urban Environment of Basra City, Southern Iraq

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Abstract:

The present study aims to analyze the spatial and seasonal variations in levels of petroleum hydrocarbons at the urban environment of Basra City. This is made by determination of their concentrations in water, ambient air, and soils. Several samples were collected from different sampling stations during 2009. The determination of hydrocarbons in water samples was carried out using the procedure of UNESCO, and the hydrocarbons in ambient air were measured by the portable gas detector of Drager CMS, whereas the determination of hydrocarbons in soils was conducted as described in Al-Saad. The findings demonstrated that seasonal variations in hydrocarbon concentrations which were increased during winter for both water and soil samples, while increased during summer for ambient air samples. Moreover, there were spatial variations in hydrocarbon concentrations which were significantly higher at the sampling stations located within the urban center in comparison with those in the suburbs. The recorded values were ranged from 0.11 to 190.5 µg/l in water samples, from ≥ 20 to 29.3 ppm in ambient air samples, and from 0.56 to 41.58 µg/gmdry weight in soil samples. Some concentrations lies within high levels of exposure, which may give rise to adverse health consequences.

Keywords:

Petroleum Hydrocarbons, Contamination, Water, Ambient Air, Soil, Urban Environment.

الخلاصة :

تهدف هذه الدراسة إلى تحليل التباين المكاني والفصلي لمستويات التلوث بالهيدروكربونات النفطية في البيئة الحضرية لمدينة البصرة، وذلك عبر تحديد تركيزاتها في كل من الماء والهواء المحيط ورواسب التربة. تم جمع العينات خلال العام 2009 عبر محطات مختلفة. وتم تحديد الهيدروكربونات في المياه بإتباع طريقة اليونسكو، وقيست الهيدروكربونات في عينات الهواء الجوي بجهاز كاشف الغازات المحمول نوع Drager CMS، فيما جرى تحديد تركيز الهيدروكربونات في التربة بحسب الطريقة التي وصفها السعد. أظهرت النتائج وجود تباين فصلي في تركيزات الهيدروكربونات حيث تزداد خلال الشتاء في كل من الماء والتربة وخلال الصيف في الهواء. وهناك تباين مكاني أيضاً، حيث ترتفع التركيزات بشكل ملحوظ في المواقع الواقعة داخل المدينة قياساً بتلك الواقعة في ضواحيها. وتتراوح الأقيام المسجلة للهيدروكربونات من 0.11 إلى 190.5 مايكغم/لتر بالنسبة لعينات المياه، وأقل من 20.0 إلى 29.3 جزء بالمليون بالنسبة لعينات الهواء، ومن 0.56 إلى 41.58 مايكغم/غم وزن جاف بالنسبة لعينات التربة. تقع بعض التراكيز ضمن مستويات تعرض عالية، مما قد يسبب تداعيات صحية سلبية.

Introduction :

Contamination by petroleum hydrocarbons is a harmful aspect of environmental pollution that adversely affect on public health. Thus, it is necessary that levels of hydrocarbons in an environment to be determined, particularly in areas which be rich in oil and petroleum such as Basra, Southeast Iraq. High concentrations of hydrocarbons can lead to acute environmental contamination whether in water, air, or soil that harms living organisms.

Petroleum hydrocarbons are a class of diverse organic compounds containing two or more fused aromatic rings of carbon and hydrogen atoms. They are ubiquitous environmental contaminants found in air, water, and soil. At ambient temperatures, hydrocarbons are colorless to yellow solids. The general characteristics common to the class are their high melting and boiling points, low vapor pressures, low water solubility, and high lipid solubility; their water solubility tends to decrease with increasing molecular mass. Among the several hundred different hydrocarbons already identified, 16 are considered as priority because they are supposed to be more harmful than the others; there is more information available on them and there is a greater possibility of people being exposed to them. These hydrocarbons (also called as PAHs) include the following: acenaphthene, acenaphthylene, anthracene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*ghi*]perylene, benzo[*k*]fluoranthene, chrysene, dibenz-[*a,h*]anthracene, fluoranthene, fluorene, indeno[*1,2,3-c,d*]-pyrene, naphthalene, phenanthrene, and pyrene (Anyakora, 2007).

Hydrocarbons are formed from the combustion of fossil fuels and organic matter and are ubiquitous to the environment. Anthropogenic activities are the major sources of emission of hydrocarbons into the environment, although some are released via natural processes. Studies in the past few decades suggest strongly that while genetic disposition is an important factor, nevertheless the occurrence of cancer in man is also strongly linked to environmental factors. In particular, attention has been focused on the important role played by chemical carcinogens existing in the environment. Polycyclic aromatic hydrocarbons (PAHs) represent one of the largest and most important classes of environmental carcinogens (Lee, 2001).

The objective of the present study is to determine the concentrations of petroleum hydrocarbons in the urban environment of Basra City, and to analyze spatial and seasonal variations with reference to its adverse health effects. Determination of hydrocarbon contaminates has been conducted in the terms of water, ambient air, and soil samples.

Materials and Methods:

Samples of water, air, and soil sediments were collected during different periods of 2009, and from several geographical locations within Basra City. The collection and measurement of samples have been carried out as follows:

1- Water samples: Spatially, as shown in figure (1) and table (1), water sampling stations were selected from Shatt Al-Arab river before entering into the urban area of Basra City (sample of No.1), and within the boundary of Basra City (sample of No.2), while other sampling stations represent in its creeks such as Rubat (sample of No.3), Khandak (sample of No.4), Ashar (sample of No.5), Khorah (sample of No.6), as well as Sewage Drain (sample of No.7). Tap water samples were also collected from different districts (samples of No.8,9,10, and11). Temporally, the collection of water samples was carried out for four rounds according to seasonal variation in river water levels during winter, spring, summer, and autumn.

Large samples of water (20 l) were collected from each station, with a clean amber-glass bottle of 5 liters capacity. Hydrocarbons in water were solvent extracted following the procedure of UNESCO (1976). For this, 100 ml of Nani grade carbon tetrachloride (CCl_4) was used in tow successive 50 ml extractions and the extracts were combined. The mixture was vigorously shaken to disperse the CCl_4 thoroughly throughout the water samples. Shaking was repeated several times before decanting the CCl_4. To these extracts a small amount of anhydrous sodium sulfate was added to break any emulsion and to remove excess water. The CCl_4 extracts were reduced in volume to less than 5 ml by using a rotary evaporator. The reduced extracts were carefully pipetted into a precleaned 10 ml volumetric glass, making sure any residual particles of anhydrous sodium sulfate were excluded evaporated to dryness by a stream of pure nitrogen.

Although CCl_4 is an ideal solvent for the extraction process, it is not suitable for spectroflourescence analysis; therefore CCl_4 must be replaced by a solvent, such as n-hexane which does not absorb light in the 300-400 nm range.

The flask was then rinsed with fresh hexane and the rinsing used to make the sample volume up to exactly 5 ml prior to ultraviolet fluorescence (UVF) analysis.

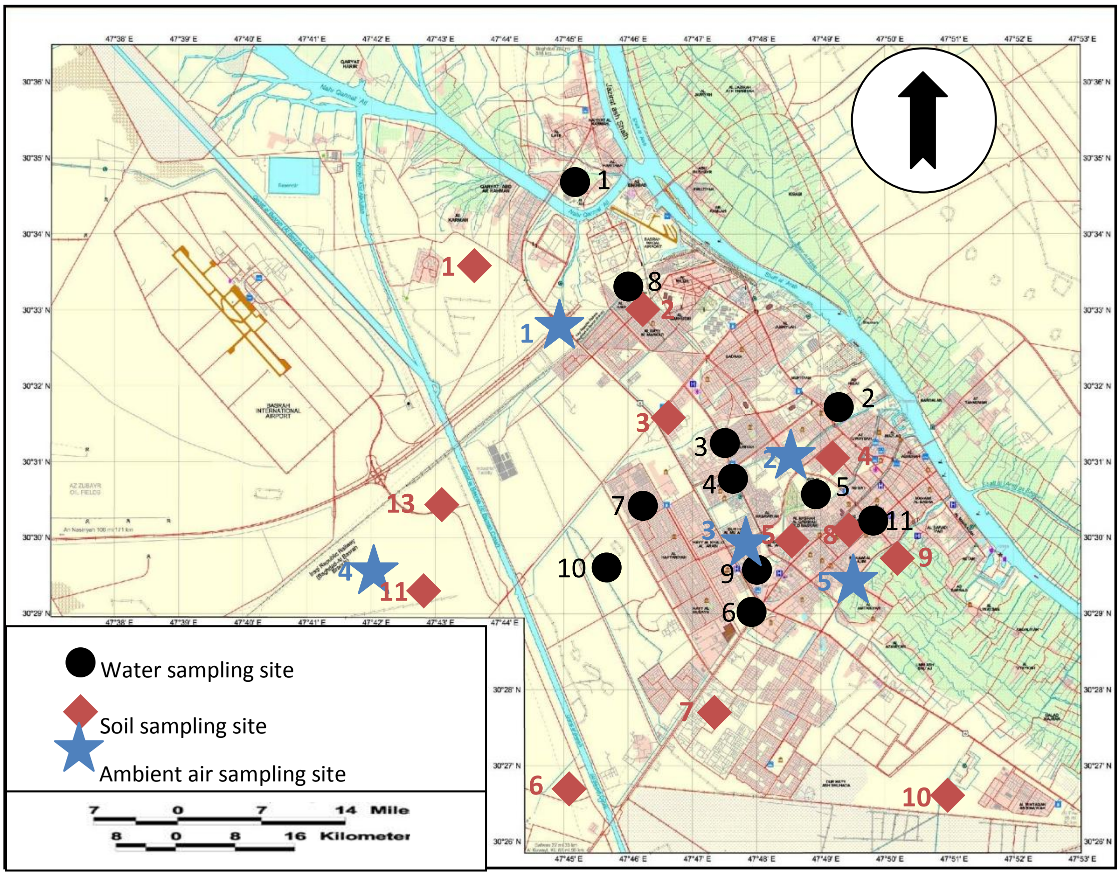

Fig. (1) Map of the study area (Basra City) and sampling stations.

2- Ambient air samples: Concentrations of petroleum hydrocarbons in air samples were directly measured in the field by using a portable gas detector of Drager CMS type, German made. This instrument is based on the spectroscopic analysis of a studied gas by means of aspirating pump a sample from ambient air and it passes through an analytical chip to be supplied with the instrument, then digitally displays the result.

Ambient air samples were seasonally measured during the winter and summer of 2009, and they're detected from five fixed stations as shown in figure (1) and table (2). These sampling stations are: 5 Miles District (sample of No.1), Ashar (Um Al-Broum) (sample of No.2), Al-Basrah Al-Qadimah (sample of

No.3), Municipal Waste Dumpsite (sample of No.4), and Baradithyah plantations (sample of No.5).

3- Soil samples: Soil samples were seasonally collected during the winter and summer of 2009. As shown in figure (1) and table (3), the collection was carried out from 12 sampling stations: Northern Gate of Basra City (Garmmat Gate) (sample of No.1), Maqal (sample of No.2), Jumhuriyah (sample of No.3), Ashar (sample of No.4), Hayyaniyah (sample of No.5), Western Gate of Basra City (AzZubyer Bridge Gate) (sample of No.6), Qublah (sample of No.7), Baradithyah (sample of No.8), Southern Gate of Basra City (Abo Al-Khaseb Gate) (sample of No.9), Hamdan Industrial District (sample of No.10), Municipal Waste Dumpsite (sample of No.11), and Point of Reference (sample of No.12).

For hydrocarbons analysis, the collected soil samples were wrapped in aluminum foil and immediately frozen -20C. Before analysis, soil samples were freeze-dried, ground finely in an agate mortar and sieved through a 62u metal (stainless- steel) sieve.

The extraction and cleanup procedure for the determination of petroleum hydrocarbons in the soil was based on that of Al-Saad (1995). Soil was placed in a pre-extracted cellulose thimble and soxhlet extracted with 150ml methanol: benzene (1:1) mixture for 24hours. At the end of this period, the extract was transferred to a storage flask and the samples were further extracted with a fresh solvent. The combined extracts were reduced in volume to 10ml in a rotary evaporator. It was then saponified for 2hours with a solution of 4N KOH in 1:1 methanol: benzene. After extracting the unsaponified matter with hexane, the extract was dried over anhydrous sodium sulfate, concentrated by a stream of N_2 for UVF analysis.

Results and Discussion:

The geographical analysis of the data obtained in the present work, it would be discussed as follows:

1- Hydrocarbons in water: Table (1) graphically represented in figure (2), shows concentrations of petroleum hydrocarbons (represented by total hydrocarbons) in water samples taken from various locations within the study area. It is clear that the recorded values demonstrate a significant seasonal variation. The concentrations of petroleum hydrocarbons in all the sampling stations were higher in winter more than those in summer, except for station No.5. As Al-Saad (1995) reported, this seasonal variation can be referred to a change in water temperature itself. Relatively low water temperatures during winter will decrease the evaporation rate of hydrocarbons, and activate microorganisms to biodegrade these organic compounds. Other environmental factors, such as adsorption by suspended solids and photo-oxidation, it may also play a major role.

Table (1) Concentrations of total hydrocarbons (µg/l) in waters of the study area, 2009.

No.	Sampling Station	Winter	Spring	Summer	Autumn
1	Shatt Al-Arab river, Garmmatt	11.3	11.06	2.65	6.58
2	Shatt Al-Arab river, Kornish	12.7	11.07	3.49	7.35
3	Rubat canal	121.2	15.96	31.9	36.3
4	Khandak canal	102.5	8.73	6.31	9.03
5	Ashar canal	37.4	8.6	56.2	6.54
6	Khorah canal	40.4	27.1	6.95	2.70
7	Sewage canal	190.5	36.6	26.6	28.2
8	Tap water, Maqal	0.44	0.34	0.26	0.28
9	Tap water, Al-Basrah Al-Qadimah	0.40	0.31	0.11	0.23
10	Tap water, Hayyaniyah	0.94	0.15	0.71	0.46
11	Tap water, Baradithyah	0.28	0.2	0.31	0.13

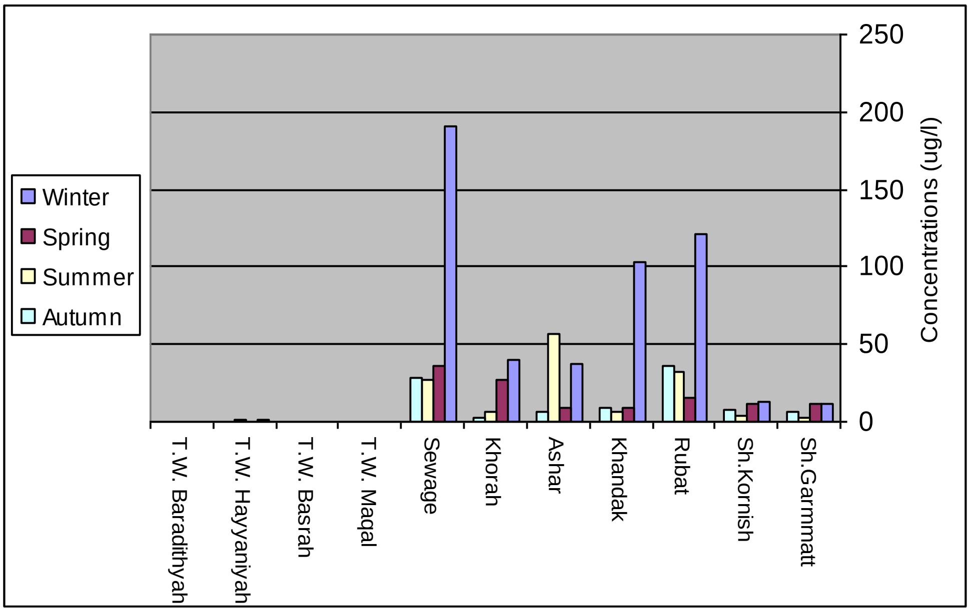

Fig.(2) Graphic representation of concentrations of total hydrocarbons (µg/l) in waters of the study area, 2009 Based on Table 1.

Concentrations of hydrocarbons in water samples were spatially varied as well. There are significant increases in the registered values at creek waters (samples of NO.3, 4,5, and 6). High contamination of these creeks may be referred to the impacts of a large variety of urban effluents which discharged into them, carrying with oils and fats from sewage, industrial, oil-exchange workshop effluents along with fuel oil spills from boats which sailed in the nearness of these creek entrances. The hydrocarbon concentration, however, in a water sample of sewage drain (sample of NO.7) was elevated even that it reached to a record value of 190.5µg/l during winter. This elevated value is due to the large quantities of oils and fats mixed with domestic washing water discharged by the studied drain.

In the Shatt Al-Arab River, the recorded level of hydrocarbons was relatively higher at the Kornish sampling station (sample of NO.2) more than at the Garmmatt sampling station (sample of NO.1), because, in addition to natural crude oil seepages, a further effect of urban pollutants on the former sampling station. This conclusion on seasonal and spatial variation in hydrocarbon concentrations is in corresponding with that of concluded by Al-Saad *et. al. (*2009a), Al-Saad (1995), Al-Imarah *et al*. (2010), Hantoush (2006).

In the relation of tap water sampling stations, hydrocarbon concentrations were significantly lower than those at fluvial sampling stations so much so that hardly seen on the chart figure (2). This has perhaps resulted in that most of hydrocarbons-absorbent particles suspended in the waters being deposited on the bottom of the settling tanks related to water supply stations, which give rise to considerable reduction in hydrocarbon concentration of tap water supplies.

Health and ecological effects of petroleum hydrocarbons are varied in the terms of a received environment. In the aquatic environment, for example, Yu (2005) reported that the potential dose of carcinogenic hydrocarbons from drinking water (assuming an average drinking water consumption of 2 l/day), ranges between 0.2 and 120 ng/day, with a median value of 6 ng/day. Drinking water concentrations have been reported to range between 0.1 and 61.6 ng/l, with most drinking water values falling between 1 and 10 ng/l. Therefore, WHO suggests that the recommended exposure standard for drinking water is 200 ng/l (Fawell and Stanfiled, 2001).

In some circumstances the water would be discolored and, possibly, would also give rise to taste and odor problems. Das (1976), for example, found that some fish such as *Tenualose illisha* catch from Shatt Al-Arab River involved in kerosene odor and repellent taste. Al-Saad and Al-Asadi (1989), reported that hydrocarbons concentrations in fish of *Aspius vorax* and *B.xanthopterus* were reached to 29.6 and 45.9 µg/gm, respectively. In addition, Al-Saad and Douabul (1984) and Al-Saad *et al.* (2009b) confirmed that hydrocarbon contaminates were accumulated in some aquatic organisms, like molluscs, lived in the Shatt Al-Arab River. While Aziz *et al.* (2000 a,b) found hydrocarbon residues even in fruits and leaves of Date Palm (*Phoenix dactylifera* L.) which irrigated from the nearby Shatt Al-Arab river.

2- Hydrocarbons in ambient air**:** Hydrocarbons to being transformed from a liquid into a gaseous phase when hydrocarbon compounds containing four or less of carbon atoms (known as volatile organic compounds or as VOCs). Automobile exhaust and fossil fuel combustion emissions are major sources of gaseous hydrocarbon emissions (Gittins, 1999).

Table (2) graphically represented in figure (3), indicates that concentrations of petroleum hydrocarbons in ambient air of the study area were considerably converging. The detected values in most of studied sampling stations were approximately 20 ppm. Elevated values recorded at only two cases: firstly, at Municipal Waste Dumpsite (sample of No.4) during summer, it was about 29.3 ppm; secondly, at Ashar (sample of No.2) during winter, it was about 26.4 ppm. The high level of violating hydrocarbons in the former may be referred to smokes emitted from the massive burning of wastes and garbage, containing plastic residues, which daily carried out at this dump site. Spellman (1999) reported that residues of plastics can consider as a likely cause to emit, when burn it, a large amount of volatile organic compounds into the atmosphere. In respect of the high level of volatile hydrocarbons in the earlier, it can be ascribed to accumulation of gaseous emissions on this hotspot as a result of automobile exhausts, smokestacks, etc. In despite of the difference between the detected values is so little, hydrocarbons concentration means during the summer was higher than that of winter (22.3 and 21.6 ppm respectively). This relative increase in hydrocarbon concentration mean during summer may be referred to raise the evaporation rate of volatile hydrocarbons due to elevated air temperatures at this season in comparison with the cold winter season, leading to the ambient air be saturated with further violate organic compounds.

Table (2) Concentrations of violate hydrocarbons (ppm) in ambient air of the study area, 2009.

NO.	Sampling Station	Winter	Summer	Mean
1	5 Miles district	20.0	20.0	20
2	Ashar, Um Al-Broum	26.4	20.2	23.3
3	Al-Basrah Al-Qadimah	20.3	20.0	20.1
4	Municipal waste dumpsite	20.0	29.3	24.6
5	Baradithyah plantations	≥ 20.0	≥ 20.0	-
6	**Average**	**21.6**	**22.3**	**22.0**

Range of the employed chip for hydrocarbons measurement is 20.0-500 ppm.

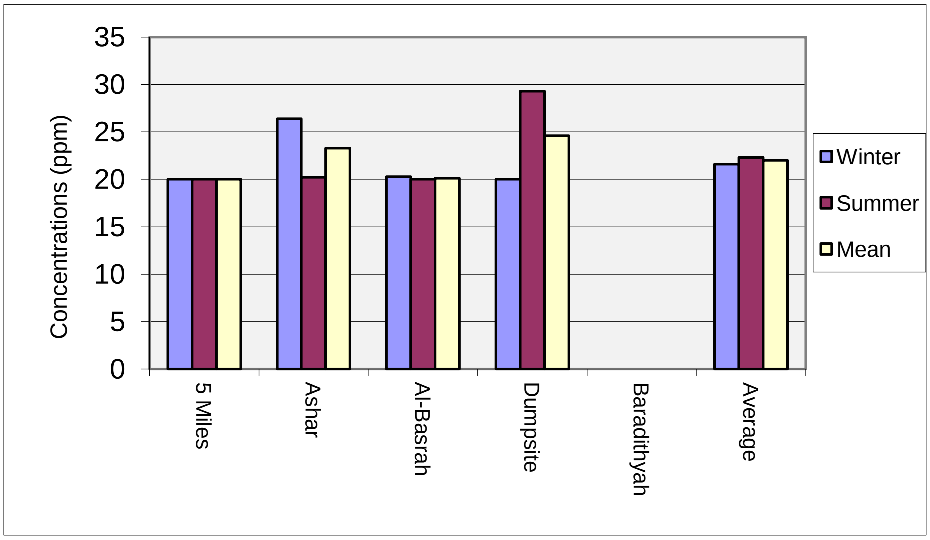

Fig.(3) Graphic representation of concentrations of volatile hydrocarbons (in ppm) in ambient air of the study area, 2009.

However, any concentration of hydrocarbons in the sampling station of Baradithyah plantations (sample of No.5), could not be detected by the instrument of Drager CMS employed in the present study (the concentration was under the sensitive level of chip, *i.e.* ≥ 20 ppm). This may due to highly dense trees and gardens in this region, which this dense vegetation acts as intake the gaseous pollutants from ambient air.

Nevertheless, average of hydrocarbon concentrations in ambient air of the study area (22 ppm) can be considered as high. One of the driving forces to this is the impact of a waste oil pool which located in the vicinity of the Basra refiner. Petroleum fluids forming-pool could be it evaporates due to increasing air temperature, transforming into violate organic compounds which give rise to atmospheric pollution, then these pollutants blow with Southern & Western South winds towards the adjacent Basra City. Studies (Issa *et al*., 1995), which carried out in Kuwait on oil pools resulted in Gulf War of 1991, found a such role in air pollution, and it was observed that violate hydrocarbon concentrations were higher during summer than winter.

The volatile hydrocarbons have an acute effect on human health, in particular. Human exposure to hydrocarbons from inhalation of ambient air varies according to the degree of urbanization, traffic and industrialization. Very high concentrations of hydrocarbons can also occur in workplaces, such as coke-oven batteries, retort houses of coal-gas works and in the metal smelting industry. Human exposure to violate hydrocarbons was estimated for a "reference man", a mean total intake of 3.12 kg^d, or 1.6% in air. Larsen and Larsen (1998) reported that volatile hydrocarbons are highly lipid-soluble and are absorbed from the lung, gut and skin, as well as they higher in humans living in an urban and industrial area than in outer suburban subjects.

3- Hydrocarbons in soils: It is often a source of hydrocarbons deposited into ground soil is an anthropogenic. Major sources are residential heating (coal, wood, oil), automobile exhaust, industrial power generation, incinerators, the production of coal tar, coke, asphalt and petroleum catalytic cracking, cooking, etc.

There were considerable spatial variations in hydrocarbons concentrations of studied samples, as shown in table (3) and figure (4). The recorded values were, for example, highest in Hamdan Industrial District sampling station (sample of No.10), which are daily depositing large quantities of oil and fuel residues spilled onto ground surface from workshops and other industrial activities. It was also observed that elevated values were found in sampling stations such as Dumpsite (sample of No.11), Qublah (sample of No.7), and Hayyaniyah (sample of 5), while the lowest values which are recorded within the urban area, it represents in Maqal sampling station (sample of No.2). Spatial variation, however, emerges more obviously when a comparison of the recorded values in inside with that of outside the urban area represented by the point of reference (sample of No.13). Certainly, this indicates to the effect of human activities, as mentioned above, leading to contaminate the urban soil rather than the unaffected lands.

Table (3) Concentrations of total hydrocarbons (μg/gm dry weight) in soil samples of the study area, 2009.

NO.	Sampling Station	Winter	Summer
1	Northern Gate on Basra City (Garmmat Gate)	9.02	7.27
2	Maqal District	1.24	2.71
3	Jumhuriyah District	11.67	7.60
4	Ashar District	10.55	15.85
5	Hayyaniyah District	23.90	7.47
6	Western Gate on Basra City (AzZubyer Bridge Gate)	2.94	3.46
7	Qublah District	36.65	7.09
8	Baradithyah District	6.52	4.33
9	Southern Gate on Basra City (Abo Al-Khaseb Gate)	4.01	3.59
10	Hamdan Industrial District	41.58	27.05
11	Municipal Waste Dumpsite	37.17	5.22
12	**Average**	**16.83**	**8.33**
13	Point of Reference	0.98	0.56

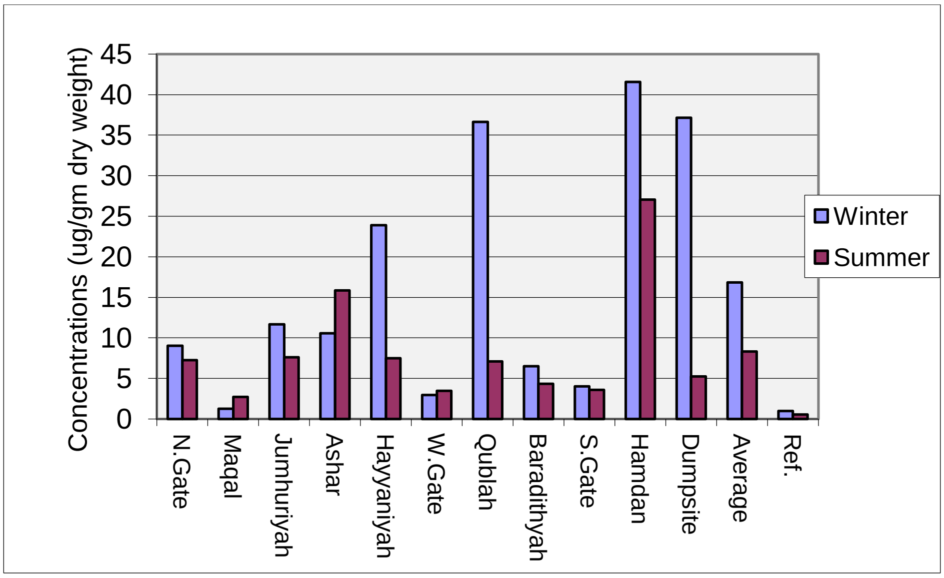

Fig. (4) Graphic representation of concentrations of total hydrocarbons (µg/gm dry weight) in soils of the study area, 2009.
Based on Table (3).

is obvious that levels of petroleum hydrocarbons in most of the studied sampling stations are higher during winter than those of summer, based on the total average. As Yaron *et al*. (1996) reported, this can be referred largely to role of which played the climatic conditions. During winter, soil temperature declined as a result of the decline in air temperatures, this acts as slow down the evaporation process of fluids from the soil surface and ground. Since increase in soil moisture during this season (as a result of rainfall, groundwater table rise, seepage, low rate of evaporation, etc.) also acts as rise to absorption ability between soil particles and fluid molecules, then hydrocarbons will prolong during the winter more than summer. It is during the summer season, violate organic compounds expose to a further accelerated evaporation as a consequence of elevated air temperatures.

To realize the environmental risk of hydrocarbon contaminates accumulated in the soil of the study area, it is the recommended exposure standard (10 µg/gm dry weight) demonstrate that, as shown in figure.(4), there were excesses in some of sampling stations, particularly during winter (as in Jumhuriyah, Hayyaniyah, Qublah, Dumpsite), while Hamdan Industrial District and Ashar suffers from hydrocarbon contamination both during summer and winter.

By comparison, the levels of hydrocarbons in soils of British cities have ranged from 0.43 to 5.39 µg/gm dry weight (Merrington *et al*., 2010), while the recorded level in Basra City (based on the present study) is ranged from 8.33 to 16.83 µg/gm dry weight. As implied from above comparison, the difference is very big.

The soils contaminated by petroleum hydrocarbons have considerable risks. They cling to sediments and soil, are difficult to degrade, can bioaccumulate in fat, and are toxic; that is, they are persistent, bioaccumulative, and toxic (Hill, 2004).

Conclusion:

Petroleum hydrocarbons contamination affects the urban environment of Basra City in the terms of waters, ambient air, and soils. Anthropogenic activities are the major sources of emission of hydrocarbons into that environment. Hydrocarbons concentrations in some samples were high, so that will reduces the beneficial use of water and soil resources as well as the health of ambient air, which may give rise to adverse health consequences.

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