Marsh Bulletin Issue 20 Volume 1 (April 2025): 12-18

MARSH BULLETIN
EISSN 2957-9848

Evaluation of Total Petroleum Hydrocarbons in Soils of Basrah City

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Abstract
Basrah city suffers from pollution with petroleum hydrocarbons which are toxic to human and the environment. In the current study the concentrations of total petroleum hydrocarbons (TPHs) were estimated in soils of Basrah city. The study area was included thirty stations distributed in eight locations (five residential areas, four oil areas, four agricultural areas, five roads, four petrol stations, two power plants, two public parks and four areas near private electrical generators) during dry and wet periods (from July 2019 to March 2020). The mean concentrations of TPHs during the study period in all locations were ranged from 8.00 µg g^{-1} dry weight in agricultural areas to 265.11 µg g^{-1} dry weight in roads. The mean concentrations of TPHs in the dry period were ranged from 6.13 to 189.92 µg g^{-1} dry weight, while in the wet period were ranged from 9.87 to 340.29 µg g^{-1} dry weight. It was concluded that oil refineries are the main cause, in addition to other sources of hydrocarbons in soil pollution with petroleum hydrocarbons in Basrah city.

Keywords: TPHs, soil, pollution, basrah, Iraq

Received 11/2/2025 Accepted 18/3/2025 Published 4/4/2025

Introduction

Petroleum hydrocarbons is one of the important environmental problems in some areas, particularly around petroleum refineries and fuel stations (Al-Ali *et al*, 2016)

Hydrocarbons are harmful pollutants that release from anthropogenic sources such as transport, settlement, and industrial development (Banan *et al*., 2018; Jaruga *et al*., 2020) as well as from natural sources such as volcanic eruptions, forests burning and decaying organic matter. These serious compounds accumulated in urban and sub urban soil can be transfer to the environment through precipitation and urban runoff, released into air by volatilization, and carried into yield via roots from polluted soil, that may indirectly pollute water, air, and food (Zeng *et al*., 2009; Bortey-Sam *et al*., 2014).

A hydrocarbon can be defined as chemical compound which composed of Carbon (C) and Hydrogen (H) elements (Elkelawy and Eldin, 2018). The main sources of soil pollution with petroleum hydrocarbons are from emission of pollutants during accidents or human activities into the environment as well as natural sources (Bardi *et al*. 2000; Agarwal, 2009).

Crude oil pollution causes to soil structure disorder. Its leads to lack of organic matter contents, soil minerals, soil nutrients, soil fertility, and bad crop yield. It also leads to leaching and erosion of soil (Palese *et al*., 2003; Nwaichi *et al*., 2014). Exposure to crude oil and oil products causes direct and indirect human health risk. Direct exposures to hydrocarbons compounds include inhalation contaminated air with volatile hydrocarbons compounds and direct dermal contact, whereas indirect exposures are due to ingestion or drinking contaminated food and water **(**Kuppusamy *et al*., 2020).

Basrah city suffers from severe pollution with petroleum pollutants, especially hydrocarbon compounds due to the presence of oil fields, the increase in drilling, exploration to extract oil and due to its refining operations, the accompanying emissions of pollutants and oil spills, in addition to soil direct pollution, it receives pollutants from the water through leaching and from air through precipitation and considering that water and air are essential components of the soil. In addition to the oil fields, Basrah exposed annually to tons of residues resulting from the combustion of gasoline in vehicles, as well as power plant stations, fuel stations and private electrical generators. All these sources caused severe pollution with hydrocarbons, which have harmful impacts on the people and environment. The purpose of this study is to evaluate the concentrations of total petroleum hydrocarbons (TPHs) in the soil samples taken from different regions along Basrah city.

Materials and Methods

Study area

Basrah city is the third largest city in Iraq in terms of population (2.532 million people) and the sixth largest in Iraq in terms of area (19,070 km^2). Economically, Basrah city is the economic capital of Iraq that includes the biggest oil fields, including the Al-Rumaila field and the Al-Shuaiba fields (Al-Saad *et al*., 2019). It has many ports and industries. It located in the fertile plains of Mesopotamia therefor it is considered as one of the main centers of agriculture, also it is considered as a tourist city.

The studied stations are distributed from north to south at Basrah city, divided into thirty stations distributed in eight locations that included (five residential areas, four oil areas, four agricultural areas, five public roads, four petrol stations, two power plants, two public parks and four near private electrical generators) as shown in Figure 1.

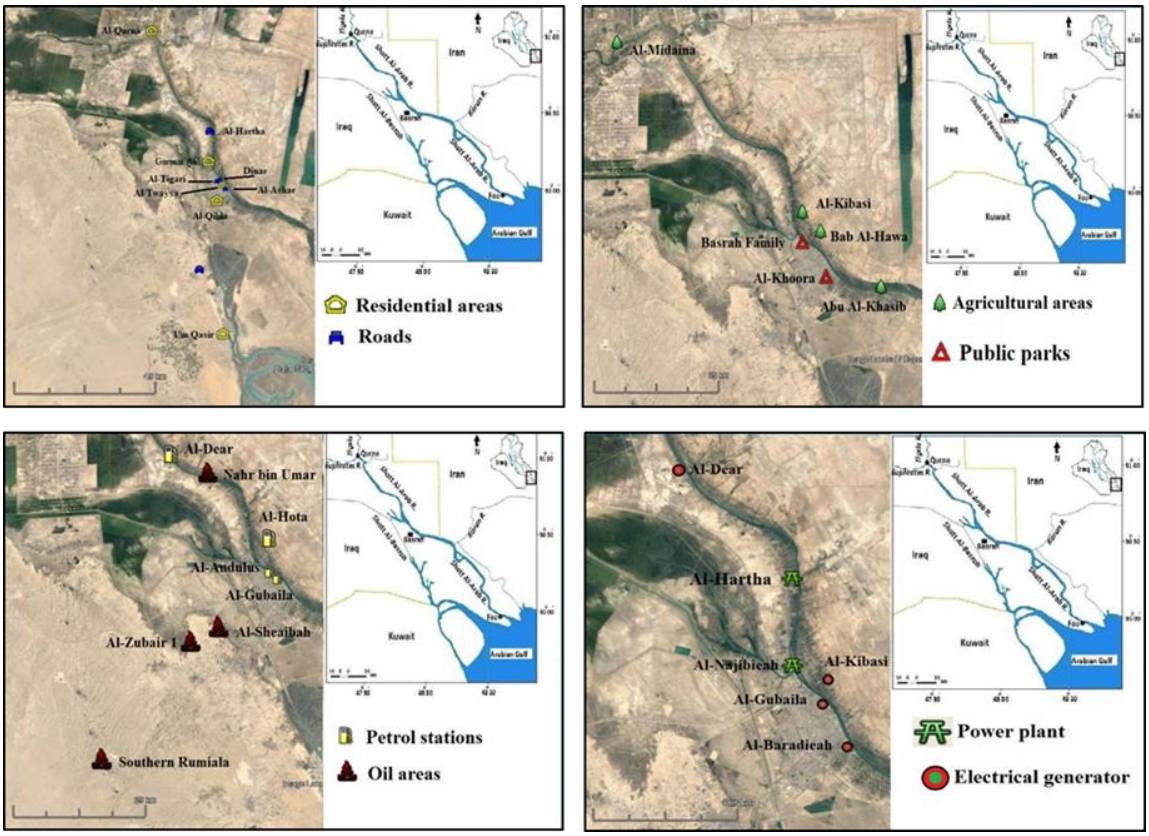

Figure 1: Maps of the study areas.

Soil sampling analysis

Soil samples were taken during two periods the dry period (July, August and September 2019) and wet period (December 2019, January, February and March 2020) from topsoil in depth 0-15 cm using stainless steel shovels. The soil samples taken from 3-5 random sites within each station, mix together as a composite sample and placed in aluminum foil wraps, then the soil samples air- dried at room temperature and sieved through 2 mm mesh sieve.
Dried soil samples were grinded finely by using a mechanical mortar, sieved with a 63 µm mesh sieve and stored in glasses containers until analysis to measure the hydrocarbons according to (Goutx and Saliot, 1980). Twenty grams of each sample were put in thimble and extracted using Soxhlet intermittent extraction with mixed organic solvents (100 ml) methanol: benzene (1:1 v/v) for 48 hrs. at temperature below 40C°. The combined extracts were saponification for 2 hrs using (15ml) 4M MeOH (KOH) at the temperature doesn't exceed 40 C°, cooled at room temperature. Hydrocarbon compounds were extracted with n-hexane (50 ml) using separator funnel. The upper unsaponification fraction with hexane (hydrocarbons) was passed through glass column with length 20 cm. (the bottom packed with glass wool, then about 10 g deactivated silica gel (100-200 mesh), 10 g deactivated alumina (100-200 mesh), and 5g anhydrous sodium sulfate (Na_2SO_4) at the top). The aliphatic fraction (n-alkanes) was eluted from the column using n- hexane (40 ml), while the aromatics were eluted by benzene (40 ml). Each sample were evaporated using a rotary evaporator, stored until detection with spectrofluorometer instrument to determine the total petroleum hydrocarbons (TPHs) in soil samples.

Results

The concentrations of total petroleum hydrocarbons (TPHs) of each station during the dry and wet periods were shown in Figures 2 and 3.

In the dry period the concentration of TPHs in soil at residential areas ranged from 7.42 µg g^{-1} dw in Um Qasir to 82.92 µg g^{-1} dw in Al-Twaysa, whereas in oil areas ranged from 73.06 µg g^{-1} dw in Al-Shiaaba to 277.07 µg g^{-1} dw in Al- Southern Rumaila, but in agricultural areas ranged from 3.19 µg g^{-1} dw in Al-Kibasi to 11.33 µg g^{-1} dw in Abu Al-Kasib. In roads soil TPHs ranged from 103.78 µg g^{-1} dw in Dinar Street to 363.58 µg g^{-1} dw in Kour Al-Zubair, while in petrol stations ranged from 10.09 µg g^{-1} dw in Al-Hota to 225.11 µg g^{-1} dw in Al-Gubaila, but in power plants ranged from 29.73 dw µg g^{-1} in Al-Hartha to 138.80 µg g^{-1} dw in Al-Najibia. In public parks ranged from 13.30 µg g^{-1} dw in Basrah Family to 20.93 µg g^{-1} dw in Al-Khoorah, while in electrical generators ranged from 8.25 µg g^{-1} dw in Al-Kibasi to 137.85 µg g^{-1} dw in Al-Baradieah.

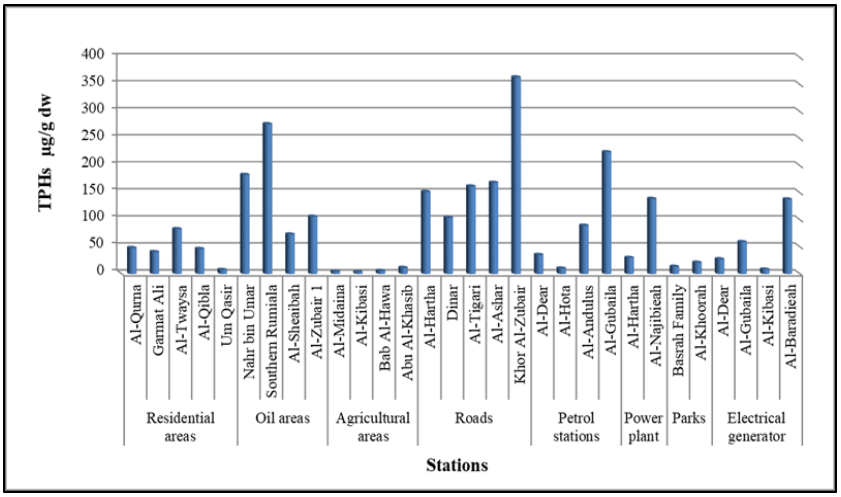

Figure 2: Soil TPHs concentrations (µg g^{-1} dw) in soil of the studied stations during the dry period.

In the wet period the soil TPHs concentrations in residential areas ranged from 10.28 µg g^{-1} dw in Al-Qibla to 205.85 µg g^{-1} dw in Al-Qurna, whereas in oil areas ranged from 17.92 µg g^{-1} dw in Al-Shiaaba to 283.18 µg g^{-1} dw in Al- Southern Rumaila, but in agricultural areas ranged from 6.70 µg g^{-1} dw in Al-Kibasi to 15.93 µg g^{-1} dw in Abu Al-Kasib. In roads soil TPHs ranged from 82.14 µg g^{-1} dw in Al-Ashar to 1266.60 µg g^{-1} dw in Dinar Street, while in petrol stations ranged from 9.51 µg g^{-1} dw in Al-Dear to 25.35 µg g^{-1} dw in Al-Andulus, but in power plants ranged from 41.34 µg g^{-1} dw in Al-Hartha to 83.18 µg g^{-1} dw in Al-Najibia. In public parks ranged from 34.12 µg g^{-1} dw in Al-Khoorah to 108.43 µg g^{-1} dw in Basrah Family, while in electrical generators ranged from 4.33 µg g^{-1} dw in Al-Kibasi to 154.70 µg g^{-1} dw in Al-Gubaila

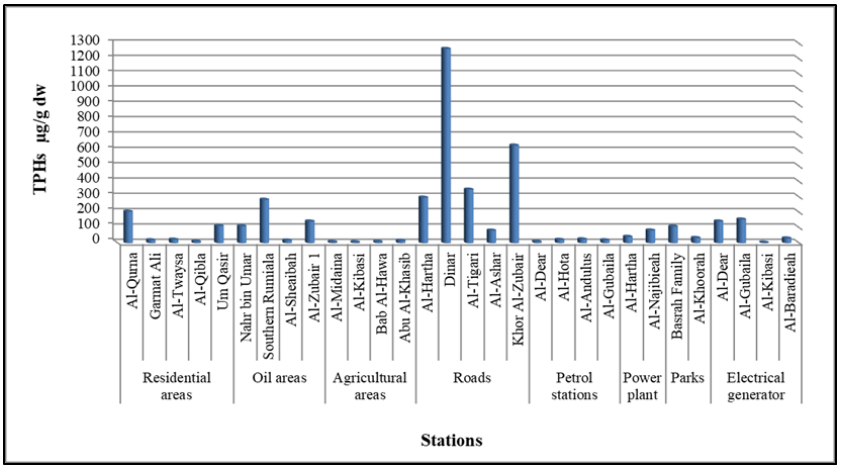

Figure 3: Soil TPHs concentrations (µg g^{-1} dw) in soil of the studied stations during the wet period.

The annual concentrations mean of TPHs during the study period in all locations as shown in Table 1. The lowest concentration of TPHs 8.00 µg g^{-1} dw was recorded in agricultural areas, whereas the highest concentration 265.11 µg g^{-1} dw was recorded in roads. The mean concentrations of TPHs were ranged from 6.13 to 189.92 µg g^{-1} dw in the dry period, while in the wet period were ranged from 9.87 to 340.29 µg g^{-1} dw.

Table 1: The annual concentrations of TPHs (µg g^{-1} dw) during the study period in all locations.

Locations	TPHs (µg g^{-1} dw)		Annual mean of TPHs (µg g^{-1} dw)
	Dry period	Wet period	
Residential areas	45.02	74.22	59.62
Oil areas	159.81	138.42	149.12
Agricultural areas	6.13	9.87	8.00
Roads	189.92	340.29	265.11
Petrol stations	89.93	19.07	54.50
Power plants	84.26	62.26	73.26
Public parks	17.11	71.28	44.20
Electrical generators	58.06	83.05	70.56
Min	**6.13**	**9.87**	**8.00**
Max	**189.92**	**340.29**	**265.11**
Mean	**81.28**	**99.81**	**90.54**
SD	**65.11**	**104.94**	**80.90**

Statistical analysis (ANOVA-one way) showed significant differences (P<0.05) for TPHs in the dry period, but non-significant differences (P>0.05) in the wet period among locations. There were non-significant differences (P>0.05) between periods in all locations.

Discussion

Total petroleum hydrocarbons are organic compounds that one of toxic environmental pollutants (Al-Halfy *et al*., 2021). The higher values of TPHs in current study were recorded in roads and oil areas, whereas the lower values were recorded in agricultural areas. The soil contamination with TPHs is due to industrial, agricultural and domestic activities Al-Ali *et al*, (2016). The reason for the increasing of TPHs in the studied locations is due to the discharging of petroleum wastes from refined oils, gas production plants, natural gas flares transportation, power plants and private electrical generators in addition to vehicle emissions, also the extraction and production of crude oil in oilfields (Al- Saad *et al.*, 2015; Karem, 2016; Kahdim, 2019). The decreasing of TPHs in agricultural areas is due to the far these areas from the petroleum sources, or because of that plant's uptake these compounds (Košnář *et al*., 2018). The studies stresses that the greatest risk in the future is related to the increase of petroleum hydrocarbons pollution which may appear in soils near express ways (Badowska and Bandzierz, 2019. There were differences in values of TPHs between the dry and wet period, the values in the dry period were higher than in the wet period in some station, whereas the others the values in the wet period were the highest. It was a significant correlation between TPHs and soil moisture in the dry period ($r = -0.524$, $p < 0.01$) and wet period ($r = -0.409$, $p < 0.05$). The result in some stations agrees with previous studies for Douabul *et al.*, 2012, Karem, 2016 and Al-Hassen, 2011, Kahdim, 2019, who found that the concentrations of TPHs were higher in winter than in summer, but the result in other stations disagrees with previous studies, Table 2.

This is may be due to the climate which is hot and dusty in summer that led to increase the deposition of compounds from atmosphere to soil (Al-Rudaini *et al*., 2019) or may be due to increasing of usage of the private electrical generators which add large quantities of TPHs in soil. The value of TPHs was very high in roads in the wet period, this is because of tire burning in many roads, near oil companies and near Um Qasir port in Basrah city during demonstrations in October revolution during the study periods that put out large quantities of hydrocarbons in soil.

Table 2: Comparing the soil TPHs (µg g^{-1}dw) in the current study with previous studies.

Study area	TPHs µg g^{-1}dw	Reference
Basrah city	8.33 – 16.83	Al-Hassen (2011),
Basrah city	13.0 - 38.8	Douabul *et al.*, (2012)
Basrah city	2.2 - 75.05	Al-Ali *et al*, (2016)
West Qurna-2 Oil Field	16.66 - 37.37	Karem (2016)
West Qurna-1 Oil Field	9.52 - 31.04	Kadhim (2019)
Rumaila Oil Field	0.5 – 93.95	Al-Halfy *et al*., 2021
Basrah city	8.00 – 265.11	Current study

Conclusions

The analysis of Basrah city soils showed that the highest values of TPHs in current study were recorded in roads and oil areas, whereas the lowest values were recorded in agricultural areas. Generally, the concentrations levels of TPHs in the current study were higher than in the previous studies in Basrah city, this may be due to the continuous discharging of petroleum wastes from refined oils, gas production plants, natural gas flares transportation, power plants and private electrical generators in addition to vehicle emissions, also the extraction and production of crude oil in oilfields.

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تقييم الهيدروكربونات البترولية الكلية في تربة مدينة البصرة.

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المستخلص
تعاني مدينة البصرة من التلوث بالهيدروكربونات البترولية، وهي سامة للإنسان والبيئة. في هذه الدراسة، تم تقدير تراكيز إجمالي الهيدروكربونات البترولية (TPHs) في تربة مدينة البصرة. شملت منطقة الدراسة ثلاثين محطة موزعة على ثمانية مواقع (خمس مناطق سكنية، أربع مناطق نفطية، أربع مناطق زراعية، خمس طرق، أربع محطات وقود، محطتان لتوليد الطاقة، حديقتان عامتان، وأربع مناطق قريبة من مولدات كهربائية خاصة) خلال فترات الجفاف والرطوبة (من يوليو 2019 إلى مارس 2020). تراوحت متوسطات تركيزات الهيدروكربونات البترولية (TPHs) خلال فترة الدراسة في جميع المواقع بين 8.00 ميكروغرام/غرام ونصف من الوزن الجاف في المناطق الزراعية و265.11 ميكروغرام/غرام ونصف من الوزن الجاف في الطرق. وتراوحت متوسطات تركيزات الهيدروكربونات البترولية في فترة الجفاف بين 6.13 و189.92 ميكروغرام/غرام من الوزن الجاف، بينما تراوحت في فترة الأمطار بين 9.87 و340.29 ميكروغرام/غرام من الوزن الجاف. وخلصت الدراسة إلى أن مصافي النفط هي السبب الرئيسي، إلى جانب مصادر أخرى للهيدروكربونات، في تلوث التربة بالهيدروكربونات البترولية في مدينة البصرة.

الكلمات المفتاحية: الهيدروكربونات الكلية، تلوث التربة، البصرة، العراق