Journal of Biology, Agriculture and Healthcare www.iiste.org
ISSN 2224-3208 (Paper) ISSN 2225-093X (Online)
Vol.6, No.12 2016

Petroleum Hydrocarbons in Water, Soil and Tomato Plant (Lycopersican esculentum L.) at Basra City, Iraq

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Abstract:
This study focused on the determination of Total Petroleum Hydrocarbons (TPH) concentration in soil, water and tomato plant *Lycopersican esculentum L.* at (root , stem, and leaf) and biomass of these plant in four stations Safwan , shuaiba , Abu Al-kasibe and Garma Ali at Basra city, Iraq. The result show that higher concentrations of (TPH) in the soil and water of Safwan than other stations related to industrial , agricultural and domestic activities which released to environment contaminated to the ground water. The result also show variation in (TPH) between *Lycopersican esculentum* parts (root , stem and leaf) , the higher concentration was found in tomato root of Safwan station compare to other stations and this level was highest than other parts of plant in the same station and other stations. There was positive correlation between petroleum hydrocarbons in soil and plant parts indicated that the plants obtained the TPH from the soil. The total nitrogen was high levels (2.31mg/l) in tomatoes plant in Garmat Ali station while the lowest levels (1.33mg/l) was in shuaiba station . Total phosphorus was higher in Abu kasibe (0.25mg/l) and low levels (0.11mg/l) in Safwan. The percentage of dry mass observed in this order Abu kasibe > Garma Ali > Safwan > shuaiba . The bioconcentration factor (BCF) and Translocation factor (TF) which is very important parameters to check the ability of plants for phytoremediation have been calculated.

1. Introduction:

Hydrocarbon contamination in the environment is a very serious problem whether it comes from petroleum, pesticides or other toxic organic matter. Environmental pollution caused by petroleum is of great concern because petroleum hydrocarbons are toxic to all forms of life. Environmental contamination by crude oil is relatively common because of its widespread use and its associated disposal operations and accidental spills. The term petroleum is referred to an extremely complex mixture of a wide variety of low and high molecular weight hydrocarbons (Bishop , 1997 ; Abha and Singh , 2012) . This complex mixture contains saturated alkanes, branched alkanes, alkenes, napthenes (homo-cyclics and hetero-cyclics), aromatics (including aromatics containing hetero atoms like sulfur, oxygen, nitrogen, and other heavy metal complexes), naptheno-aromatics, large aromatic molecules like resins, asphaltenes, and hydrocarbon containing different functional groups like carboxylic acids, ethers, etc. Crude oil also contains heavy metals and much of the heavy metal content of crude oil is associated with pyrolic structures known as porphyrins . (Abha and Singh , (2012)

Over Two million tons of oil produced in the world, The pollution of soil and groundwater resources with hydrocarbons around oil refineries and the vicinity of fuel transportation facilities are considerable challenge of environment pollution issue. Mentioned Petroleum hydrocarbons naturally are in various chemicals used by human activities such as fuel of vehicles and warming homes. Spilled and leaked Crude oil fill soil pores by moving vertically with capillary forces and gravity in the unsaturated soil. Large amount leakage can reach water level and then accumulated and move to groundwater as its specific gravity less than water will float in the water. Total Petroleum Hydrocarbons (TPHS) mostly contaminate environment due to inherent ability, such as solubility, volatility, and their biodegradable they also identified toxic for animal. (Vaziri et al., 2013).

In the environment, petroleum component mixtures are subject to weathering effects such as volatilization, biodegradation, partitioning into water, oxidation, and photodegradation. These effects change the distribution of components in a mixture and change the chemical composition of components as well (Bishop , 1997) .

Petroleum contamination of soil is a widespread and well recognized global environmental issue (Rayner et al., 2007)

The stability of these pollutants at the soil and gradually accumulating over time disrupt the normal function of the soil, such as reduced agricultural capability (Vaziri et al., 2013).

Soil contamination can result in soil degradation, bring great loss to agricultural production and pose threat to human health. Many of the soil contaminants are petroleum hydrocarbons (PHCs) derived from crude oil or refined petroleum products (Yan , 2012)

The consequences of the aforementioned factors that lead to environmental hazards need to be remedied. Phytoremediation is the in-situ use of plants and their associated microorganisms to degrade, contain or render harmless contaminants in soil or groundwater (Raimi and Isichei , 2015)

Karenlampi et al. (2000) reported four characteristics that makes a plant suitable for phytoremediation, these include: (i) the plant's ability to accumulate extracted pollutant; (ii) plants should have enough tolerance to be able to not only survive in polluted soils, but to carry pollutants within their stems; (iii) the species should be fast growing with an amplified ability to accumulate toxins; and (iv) the plant should be easily harvestable for simple disposal

The oil pollution in Basra / Iraq being widespread , because its richness in oil wells as the Drilling and extraction of oil leads to environmental pollution specially soil pollution with petroleum hydrocarbons compounds . In addition to surface water, ground water, and live organisms existing pollution in the environment, especially plants, including economic plants grown on farms located near the oil wells which affects the productivity of those plants. In this work we aimed to determine the total petroleum hydrocarbon in soil , ground water and in tomatoes plant (root , stem and leaf) in addition to plant contents of nitrogen and phosphors and productivity of dry mass in southern Basra city .

2. MATERIAL AND METHOD

2.1 .Collection of Samples and extraction

The soil samples were collected 50 cm subsurface from four station (Garmat Ali (Agricultural research station of university) , Safoan , Shuaiba , Abu Al-Kasibe,) .Samples were dried and the analysis of these samples were done according to method of (Goutex and Saliot, 1980) established by (IOC/ WMO , 1982) . Plant samples were collected from the leaf, stem and root of Tomato (*Lycopersican esculentum*). then freeze dried and extraction of these samples were done according to method of (Grimalt and Oliver , 1993) . Water sample collected from irrigation water of the study stations, total petroleum hydrocarbons extract and determined using method described by (UNEP , 1989) All samples were determined by using spectroflourometer type (Shimadzu RF-540) ,Emission range (290-410 nm) while Excitation (360nm)

Total nitrogen and phosphors determine using oxidative methods by digestive acids with mixture of 4% perchloric acid to sulfuric acid as describe by (Gresser and Parson , 1979) .The total nitrogen determine using Kjeldahl method, while Plant biomass determined by Lind , (1979) method by weighting plant before and after drying (103) ˚C

2.2 .Bioconcentration Factor

The phytoremediation potential of *Lycopersican esculentum* was examined by using bioconcentration factor according to (Agoramoorthy et al., 2008).

$$BCF=C_{biota}/C_{soil}$$

Where C biota was the chemical concentrations in the taxa from
this study and C soil was the chemical concentration in the soil.

2.3 Translocation Factor

Translocation ratio or translocation factor (TF) was calculated to understand the mobility potential of petroleum hydrocarbon from root to leaf or from root to stem. The following formula was used to calculate the translocation ratio (Mattina et al., 2003; Yoon et al., 2006; Pahalawattaarachchi *et al*.,2009 Agamuthu and Dadrasnia , 2013)

$$TF=C_{leaf\ or\ stem}/\ C_{root}$$

Where C leaf or stem is the concentration of TPH in leaf and plant stem sample and C root is the concentration of TPH in root sample. If TF>1 this mean that translocation of any pollutant effectively was made to the stem or leaf from root (Baker and Brooks, 1989; Zhang et al., 2002; Fayiga and Ma, 2006).

2.4 Statistical analysis

The inter relationship between the concentration of TPH in the studied samples was determined using Spearman correlation coefficient (r value) by spss program.

3 RESULTS AND DISCUSSION

3.1. Total petroleum hydrocarbon distribution in soil and water:

The concentrations of total petroleum hydrocarbons (TPH) in the soil and water show high concentration in Safwan than other station , the levels was Safwan > shuaiba > Abu Al-kasibe > Garma Ali which was (75.05 , 61.4 , 6.28 and 2.2) µ/g respectively in soil and (2.67 , 2.04 , 1.16 and 1.14) µ/l respectively in water (Table 1). There is strong correlation between TPH in water and soil (r=0.9786)

The result indicate that the contamination in Safwan was higher than other station , the contamination of Total Petroleum Hydrocarbon (TPH) is related to industrial , agricultural and domestic activities which released to environment contaminated the ground water. Soil and air. Pollution of soils with petroleum hydrocarbons is one of the important environmental problems in some areas, particularly around petroleum refineries and fuel stations (Mosaed et al., 2015) .

The result of (TPH) in this study was less than other study from other neighboring countries such as

Iran ,it ranged in Hamedan City between 2433.20- 11130.27 mg kg-1 with a mean value of 6444.08 mg kg-1 (Mosaed et al., 2015) , 50000 mg / kg in study of (Ravanbakhsh et al., 2009) and 34358±1633 mg / kg from contaminated lands in Iran recorded by (Daryabeigi Zand et al., 2010) . In Basrah city total petroleum hydrocarbons was (16.83 , 8.33) µ/g in winter and summer respectively (AL-Hassan , 2011) . and Al-Saad et al., 2015 found the average of the total identified n-alkanes concentrations in soil samples were found ranging from 03.575 to 21.266 µg g dry weight hydrocarbons in surface soils of Basrah city, southern Iraq

Table .1 Total petroleum Hydrocarbons in water, soil and plant samples in study stations

Stations	Environment sample		plant sample(µg/g)		
	Soil(µg/g)	Water(µ/l)	Leaf(µg/g)	stem(µg/g)	Root(µg/g)
Garma Ali	2.2±0.1	1.14± 0.2	25.1± 0.6	28.21±0.1	20±0.2
Safwan	75.05±1.55	2.67±0.24	21.56± 0.34	55.74± 0.21	102.63±0.23
shuaiba	61.4±1.4	2.04±0.14	43± 0.1	67.2± 0.1	98.2±0.6
Abu AL-kasibe	6.28±0.17	1.16±0.02	38.5± 0.38	32.64±0.36	24±0.56

3.2. Total petroleum hydrocarbon distribution in plant

The result in (Table 1 and Fig.1) show variation in (TPH) between *Lycopersican esculentum* parts (root , stem and leaf) , the high concentration found in tomato root of Safwane station (102.63) µg/g Comparison to other station and this level was highest than other parts of plant in the same station and other stations which was Safwane > shuaiba > Abu Al- kasibe > Garma Ali , also The concentrations of TPH in root samples in all of the sampling sites were higher than the soil and water levels . Indicating that the root have higher ability to uptake the (TPH) from the soil and irrigated water contrast with leaf samples.

While in stem and leaf the concentration was found higher in shuaiba compared with other station and the levels in stem higher (67.2) µg/g than leaf (43) µg/g the concentrations was arrange as fellows: Safwane > shuaiba > Abu Al- kasibe > Garma Ali . There were positive correlation (0.94) between petroleum hydrocarbons in soil and plant indicated that the plants obtained the TPH from the soil . The concentration of TPH in plant samples was observed in the order: root > stem > leaves. The comparison of TPH content in the plant samples shows that there is a higher uptake of TPH through root, leaf and stem samples of *Lycopersican esculentum* . Higher concentration of TPH in the root than in the leaf samples indicating more petroleum hydrocarbon pollution in the soil and transferred toward plant tissue.

This result indicate the contamination of plant with petroleum hydrocarbon especially from soil which contaminated by oil industry and from air contaminated from Oil refining that absorbed and attached by leaf and stem , and this indicate high concentration of TPH in the leaf samples due to high petroleum hydrocarbon uptake capability by leaves of the plant (Lotfinasabasl et al., 2013) .

The mean of TPH of whole plant show in Fig (2) which was high in shuaiba station (69.46) µg/g and low in Garma Ali 24.44 µg/g , so the mean of TPH concentration in root , stem and leaf compared with the mean concentration of soil in all station show in Fig (3) . The levels was higher in root and stem (61.21 , 45.95) µg/g respectively than in soil 36.23 µg/g while was lower in leaf 32.04 µg/g compared with the soil.

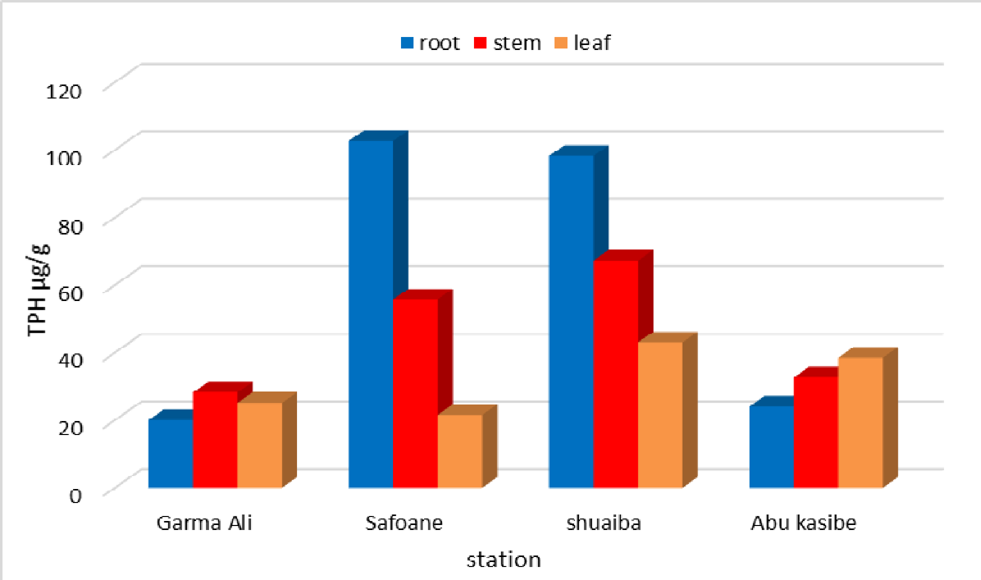

Fig 1. Total petroleum hydrocarbon in plant parts sample

The mean of TPH in this study was lower or close to other studies , (Al-Baldawi et al 2015) found the average of TPH concentration detected in *Scirpus grossus* tissue ranged between 19.86 and 91.36 mg/kg in the lower parts (roots) and 16.14 and 223.56 mg/ kg in the upper parts (stems + leaves). (Xia and Ma, 2006) implying that some of the diesel that was adsorbed in the upper parts (stems + leaves) was transported from the roots along the transpiration stream.

In Lotfinasabasl et al., (2013) study The concentration of TPH in *Avicennia marina* leaf samples ranged between 0.5- 4600 mg/kg with a mean value of 2706.7 mg/kg. TPH concentration in the root samples ranged between 0.5- 16300 mg/kg with a mean level of 4693.3 mg/kg. the average global permissible limit as (Salanitro et al , 1997)in soil (1000 mg/kg) and the phytotoxic level in the plants (1000-12000 mg/kg) while the standard levels by (Mosaed et al., 2015) in soil was (2000 mg/ kg) in this study the average in plant and soil was less than Permissible limit .

The roots of plant having more ability uptake of petroleum hydrocarbons through phytostabilization and, rhizidegradation mechanism. Phytostanilisation immobilize contaminants in the soil through the absorption and accumulation into the roots, the adsorption onto the roots, or the precipitation or immobilization within the root zone. These chemical contaminants then are rendered into a stable form. In Rhizodegradation contaminants will be degraded in the soil through the bioactivity that can be produced and exuded by plants or from soil organisms such as bacteria, yeast, and fungi. The lower concentration of TPH in leaf samples may have been caused due to phytodegradation or phyto transformation of petroleum hydrocarbons which was subjected the contaminants to the bioremedial processes occurring within the areal part of plant itself (Lotfinasabasl et al., 2013).

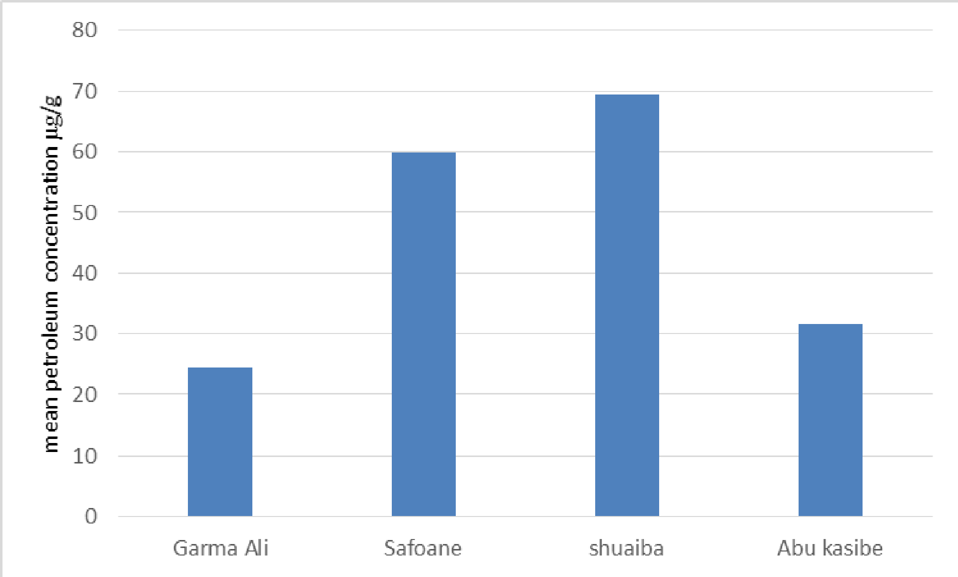

Fig.2 .mean concentration of plant Total petroleum hydrocarbons in study stations

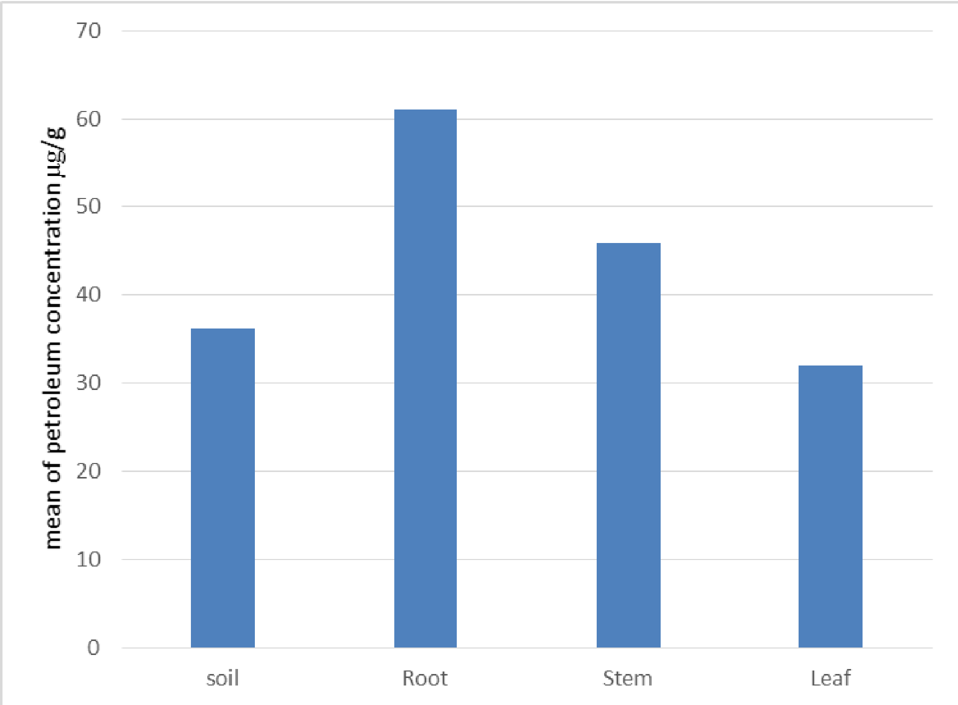

Fig 3. Means of total petroleum hydrocarbon in leaf , stem root

3.3 Effect of petroleum hydrocarbons on Total Nitrogen , Phosphorus and dry mass

The result in Table (2) show that the total nitrogen was high levels (2.31%) in tomatoes plant in Garma Ali station while the lowest levels (1.33 %) was in shuaiba station . Total phosphorus was higher in Abu kasibe (0.25 %) and low levels 0.11 % in Safwane. The percentage of dry mass observed in the order Abu kasibe > Garma Ali > Safwane> Shuaiba .

Nwankwo et al., 2014 showed that crude oil effected tomatos plant growth , he found that at higher concentration the plant cannot grow while at low concentration allow plant growth with dallied growth which indicated that the oil contamination effected crop productivity , while (Njoku et al., 2008) fond that crude oil contamination inhibits *Glycine max* (TGX 1440-1E) plant growth

Nitrogen is primarily necessary for the formation of amino acids, proteins, nucleic acids and chlorophyll. Nitrogen metabolism is mediated by an enzyme nitrate reductase located mainly in the cytoplasm of leaves of plants. It is logical to argue that conditions will impede normal nitrogen metabolism in plants and affect the synthesis of chlorophyll, the photosynthetic ability and the physiological state of the plant(Odjegba and

Okunnu, 2012).

In this study the polluted area show low nitrogen and phosphores and this effected plant growth by effected on plant dry mass .

Odjegba and Okunnu, 2012 found the inhibitory effects of crude oil on the nitrate reductase activity of *Manihot esculenta* could be attributed to the toxic nature of some of its constituents on this enzyme .

Table 2. Phosphorous,Nitrogen and dry mass% in tomato plant (*Lycopersican esculentum L.*) at different locations study.

sample	P%	N%	% dry mass
Garma Ali	**0.21±0.01**	**2.31±0.1**	**15.03±0.11**
Safoane	**0.11±0.02**	**1.82±0.04**	**13.72±0.08**
shuaiba	**0.13±0.01**	**1.33±0.01**	**12.35±0.05**
Abu AL- kasibe	**0.25±0.02**	**2.04±0.12**	**16.46±0.02**

Significant among the damages done to the environment by crude oil spills is pollution of soil which renders it less useful for agricultural activities and affects soil dependent organisms adversely (Lundstedt, 2003). Pollution of agricultural soil has in turn significantly affected the growth performance of plants. The ability of crops to germinate or grow on crude oil polluted soil is dependent on the level of crude oil spillage on soil , This means that a high level of crude oil pollution of the soil impairs germination of seedlings.**(** Ezeonu ,2012)

Many plant species are sensitive to petroleum contaminants (Huang et al. 2004). Chaineau et al. (1997) found a growth rate reduction of beans and wheat by more than 80%. Significant reduction of plant biomass by the presence of petroleum hydrocarbons has also been reported by Merkl et al.(2004). Pollution of agricultural soil has in turn significantly affected the growth performance of plants (Osuagwu et al., 2013) , they reported that soil crude oil pollution has an adverse effect on growth, yield and leaf chlorophyll content , Leaf number of air potato (*Dioscorea bulbifera*) compared with the control treatment and the reduction followed increase in crude oil intensity .Agbogidi (2011) reported that contamination of soil with crude oil significantly reduced biomass accumulation in *Jatropha curcas* when compared to seedlings grown in uncontaminated subplots. He also observed a negative interaction between soil crude oil level and weight gain in the plants. Kekere *et al.* (2011) reported that crude oil pollution negatively affected leaf number, total leaf area, plant height, stem girth, total biomass as well as crop yield in *Vigna unguiculata*. They further reported a reduced leaf chlorophyll content, nutritional composition and elevated level of heavy metal uptake in the fruits.

Ojimba and Iyagba (2012) observed that the outputs of horticultural crops were significantly reduced in crude oil-polluted farms than in non-polluted farms. They concluded that crude oil pollution had detrimental and negative effect on horticultural crops output, farm income and area of farmland cropped.

Growth depression of plants growing on soil contaminated with petroleum hydrocarbons observed by (Daryabeigi Zand et al.,2010a and b) for maize (*Zea mays* L.), tall fescue (*Festuca arundinacea*) , burning bush (*Kochia scoparia* (L.) Schard) and flax (*Linum usitatissumum* L.) , Stem heights of plant species cultivated in oil-contaminated soil were shorter than stem heights of plant species grown in clean soil.

Growing parameters of maize such as root and stem biomass, stem height, total root length, number of root tips and root depth were strongly decreased in the petroleum hydrocarbon (TPH) contaminated soil (Zamani et al., 2015) .

3.4 Bioconcentration and Translocation factors

The bioconcentration factor (BCF) and Translocation factor (TF) is very important parameters to check the ability of plants for phytoremediation (Al-Yameni et al., 2010) or to determine the quantity of petroleum hydrocarbons absorbed by the plant from the soil. This is an index of the ability of the plant to accumulate a petroleum hydrocarbons with respect to its concentration in the soil (Ghosh and Singh, 2005).

Tab(3) and Fig(4) show (BCF) and (TF) value .

Table (3) The (BCF) and (TF)values of TPH in leaf, root and stem samples at different locations study.

	BCF			TF	TF
sample	**Leaf**	**Stem**	**Root**	**(leaf/root)**	**(stem/root)**
Garma Ali	**11.41**	**12.823**	**9.091**	1.255	**1.4105**
Safoane	**0.287**	**0.743**	**1.367**	0.210	**0.543116**
shuaiba	**0.70**	**1.0945**	**1.599**	0.438	**0.684318**
Abu kasibe	**6.131**	**5.197**	**3.822**	1.604	**1.36**

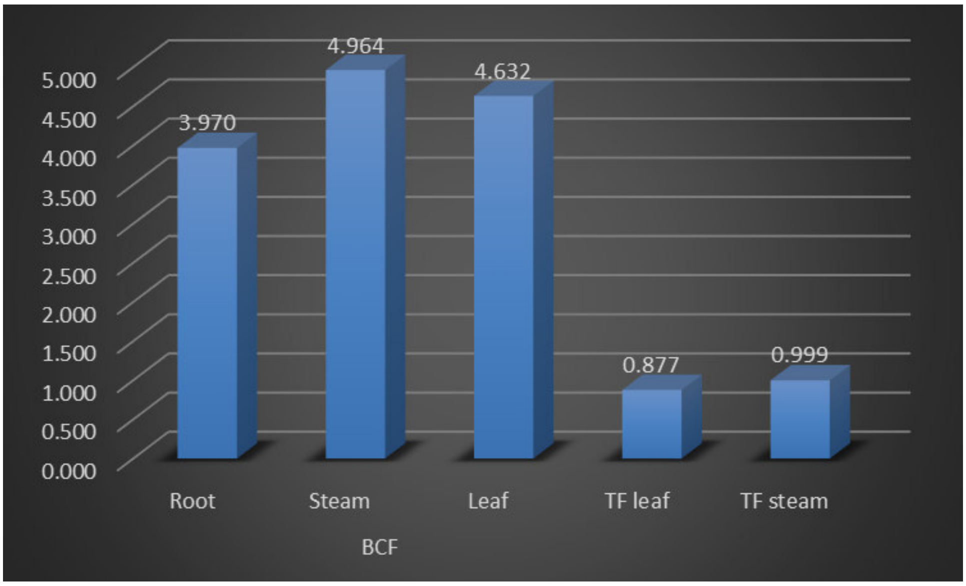

Fig.(4) mean of Bioconcentration and translocation factor of TPH in root , stem and leaf samples .

As in Table (3) There are high value of BCF in stem , leaf , root and TF in Garma Ali and Abu kasibe while in Safwane there is low BCF and TF value (less than 1) in leaf , stem and in shuaiba the low BCF value was in leaf and TF value was less than (1) ,according to Fitz and Wenzel (2002) plant exhibiting TF and BCF values less than one are unsuitable for phytoextraction . The high value of TF and BCF in this study indicates that the (*Lycopersican esculentum*) can tolerate high levels of petroleum hydrocarbons .

As (Oti , 2015) the Bioaccumulation factor is known to decrease with increasing metal concentration in the soil , so the Plants that growing at the positions that been capable of accumulating petroleum hydrocarbons in the roots , stems and leaf but most of them had low TF and BCF values, which means limited ability of petroleum hydrocarbons accumulation and translocation by the plants (Nazir et al 2013). Then in this study the relationship between petroleum hydrocarbons concentration in soil and its concentration in plant and also between them and BCF and TF in plant part show there are high capacity (positive correlation r= 0.942) to accumulate pollutants in plant parts higher than in soil or water and Low BCF and TF in plant parts (the negative significant with petroleum hydrocarbons concentration in soil r = -0.899) which can decrease with the increase of petroleum hydrocarbons in soil.

Lotfinasabasl et al., 2013 ; Siciliano and Germida , 1998 observed the higher BCF factor for root which indicates that phytoremediation occurs mostly through phytostabilisation, while the lower TF value of leaf samples shows uptake of hydrophilic compound of petroleum hydrocarbons by root and translocation to the leaf through vascular system. In general, chemicals that are highly water soluble are not sufficiently sorbet to roots or actively transported through plant membranes while the Hydrophobic chemicals which that are not soluble in water or are bound so strongly to the surface of the roots and may not pass beyond the root's surface due to the high proportion of lipids present at the surface so cannot be easily translocate into the plant(Lotfinasabasl et al., 2013) . Adesuyi et al., 2015 reported that Plants having BCF values less than one had limited ability to accumulate, translocate and phytoextract they found higher Bioconcentration Factor value greater than one of plants (*Croton lobatus*, *Borreria sp.*, *Cyathula prostrata*, *Lantana camara*, *Ficus sp.*, *Mimosa pudica*, *Eclipta prostrata*, *Commelina sp*

As a conclusion Pollution of soils with petroleum hydrocarbons is one of the important environmental problems in some areas . In the city of Basra, there are many sources of pollution due to oil production and export of oil, which lead to the pollution of the water environment, soil and air, and transmitted to the plant with nutrients and spread through the roots to the stem and leaves. In this study the concentrations of total petroleum hydrocarbons in water, soil and plant parts (root and stem and leaves) of (*Lycopersican esculentum*) , which was concentrations in soil concentration is higher than in the water and concentrations in plant parts is higher than concentrations in soil and water, and the concentrations was as the following as water <soil < leaves < stem <root the levels in stations was as the following Safwan > shuaiba > Abu Al-kasibe > Garma Ali. The bioconcentration factor (BCF) and Translocation factor (TF) estimated and the value > 1 was in Garma Ali and Abu kasibe in all parts of plant.

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