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Research Paper

Phytoremediation Of Hydrocarbon-Contaminated Soil Using Plants Adapted In Al-briga Feild- Tubriq-libya

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Abstract:
This study dedicated on the determination of Total Petroleum Hydrocarbons (TPH) concentration in soil, and some plant species at (root , and shoot), these plant were growing in Al-briga Feild oil that is located in the Krums El Khail area, the Krums El Khail located in west side of Tobruk city in area extend from east of Tobruk to Eikrama west longitude 23°49'35.14"and 23°5.'5.70" east,and latitude between 32°.5'55.77 and 32°.5'24.97"north. Results showed that there are 12 species from 8 families in study area Poaceae (27%), Polygonaceae (27%),and other families (9 %), were the most common families in this area, The result also show that higher concentrations of (TPH) presented in unplanted soils comparing with planted soils . and showed to variation in (TPH) between studied plant species parts (root , and shoot) , the higher concentration was found in root in all studied plant species,the high value in Medicago marina root(98.2 mg/kg^{-1} d.w) in fourth locations compare to other locations. There was positive relationship between petroleum hydrocarbons in planted soil and plant species parts indicated that the plants obtained the TPH from the soil.The bioconcentration factor (BCF) and Translocation factor (TF) which is very important factors to check the ability of plants for phytoremediation have been calculated. The results of TF content for the twelve species revealed that the TPH content belongs to groundparts (root).while, TF content in most plant species was lower than 1, and BCF root content was higher than 1 for all of plant species.most plant species in this study were recognized as tolerant species that can be developed to decrease soil contamination of Al-briga Feild oil . Therefore, they can be an appropriate choice for the phytoremediation of TPH Contaminated Soil.
Key words: *Phytoremediation, Total Petroleum Hydrocarbon, Contaminated Soil,plant species, Al-briga Feild oil.*

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I. INTRODUCTION:

Oil pollution is a serious issue because petroleum hydrocarbons are toxic to all life forms, and pollution from petroleum is relatively common due to its widespread use, associated disposal operations, and accidental spills. The term oil refers to a highly complex mixture of a variety of low and high molecular weight hydrocar (Bishop , 1997 ; Abha and Singh , 2012)

His compound combination includes saturated alkanes, branched alkanes, alkenes, naphthenes (homocyclic and heterocyclic), aromatics (including aromatics containing heteroatoms such as sulfur, oxygen, nitrogen, and other heavy metal complexes), naphthenoaromatics, and large aromatic molecules such as resins.

, asphaltenes, and hydrocarbons with various functional groups such as carboxylic acids, ethers, etc. Crude oil also contains heavy metals, and a significant portion of the heavy metal content of crude oil is bound to pyrrole structures called porphyrins (Abha and Singh , 2012). Large-scale environmental pollution, destruction of arable land, and harm to aquatic habitats are a few of the issues associated with the exploration and exploitation of crude oil. The majority of the issues with crude oil pollution result from unintentional discharge, sabotage, mechanical failure, loading and offloading, and improper disposal (Njoku *et al*., 2009a) increasing attention has been given to developing and implementing cutting-edge technology for cleaning up this pollutant using different remediation techniques. Phytoremediation is one such method that uses biological practices to clean up crude oil contaminated soil. Investigation has shown that numerous plants have the ability to remediate soil contaminated with crude oil (Frick *et al.*, 1999). The crude oil pollution in In Al-briga Feild 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

.While there is much evidence to suggest that plants can remediate crude oil- polluted soils, more plants need to be evaluated for their potentials to clean up crude oil-polluted. Our goal in this work is to determine the total petroleum hydrocarbons in the soil and in the studied plants (root and shoot) and to show the possibility of using these plants in the treatment of contaminated soil and which of them is suitable in the phytoremediation program.

II. MATERIAL AND METHOD

2.1 Study area

This study carried out in petroleum-polluted area of Al briga field oil is located in the Krums El Khail area, the Krums El Khail located in west side of Tobruk city in area extend from east of Tobruk to Eikrama west longitude 23°49’35.14″and 23°5.’5.70″ east,and latitude 32°.5’55.77 and 32°.5’24.97″ north. The total area about 80 hectares.(Ahmadoun&Abbas,2021).six locations, equally distributed between planted and non-planted sites. Each location was divided into 2 stands.

2.2 Collection of Samples and extraction

Twelvel plant species collected were identified according to Täckholm (1956 and 1974), Boulos (1999, 2000, 2002, 2005), Jafri and El-Gadi (1979). The identified specimens were revised in Garyounis University Herbarium based on authentic materials, and all herbarium sheets were kept in Corina Herbarium (CUGU) in Garyounis University. Plant samples were collected from planted locations in the same area,and seprated into shoots and roots. then freeze dried and extraction of these samples were done according to method of (Grimalt and Oliver , 1993) . The soil samples were collected 30 cm subsurface from planted and unplanted area in studied locations .Samples were dried and the analysis of these samples were done according to method of (Goutex and Saliot, 1980) established by (IOC/ WMO , 1982), 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).

2.3 .Bioconcentration Factor (BCF)

The phytoremediation potential of studied plant spesies was calculated using theformula outlined by Agoramoorthy *et al*.(2008) :

BCF = TBH concentration in plant root/ element concentration in soil.

2.4 Translocation Factor(TF)

the translocation factor (TF) was calculated to understand the mobility potential of petroleum hydrocarbon from root to shoot. The following formula was used to calculate the translocation ratio (Agamuthu and Dadrasnia , 2013)

TF=C shoot/ C root

Where C shoot is the concentration of TPH in shoot samples and C root is theconcentration of TPH in root samples. If TF>1 this mean that translocation of any pollutant effectively was made to the shoot from root (Fayiga and Ma, 2006).

2.5 Statistical analysis

The inter relationship between the concentration of TPH in the studied samples(plant samples and planted soil samples) was determined using Spearman correlation coefficient (r value) by spss program.also test was used to compare mean values to planted and unplanted soil and plant parts in studied locations(($P < 0.05$).

III. RESULTS AND DISCUSSION

3.1.Plant species

Results showed that there are 12 species from 8 families in study area (Table 1). Poaceae (27%), Polygonaceae (27%),and other families (9 %), were the most common families in this area. The genus *Avena* and *Polygonium* had the most frequent species in the study area. 58.33% of species were perennial while 41.66% were annual species. Chamophyte with a rate of 50% were the highest life forms(Fig.1). *Avena strerilis, Avena fatua ,Cynodon dactylon Medicago marina, Pituranthos tortuosus, Plantago lanculat, Polygonum equisetiforme* were high-densitypopulation, while, *Malva sylvestris*,and *Thymelea hirsuta* were low-density population.

Table1: List of plant species collected and identified from study area in In Al- briga Feild- Tobruk-libya.H: high-density population, M: medium-density population, L: low-density population, Th: throphyte, He: hemicryptophyte, Ch: chamophyte,and Ge: geophyte.

N	Family name	Botanical name	Commonname	Lifeform	Life cycle	Density
1	Poaceae	*Avena strerilis*	Kaphurebari	Th	Annual	H
2	Poaceae	*Avena fatua*	Kaphure	Th	Annual	H
3	Poaceae	*Cynodon dactylon*	Najem/Najel	Ge	Annual	H
4	Boraginaceae	*Echium angustifolium*	Diaget alaoraq	Ch	Perennial	M
5	Geraniaceae	*Erodium crassifolium*	Ragemashaokia	He	Perennial	M
6	Malvaceae	*Malva sylvestris*	Kubaiza	Th	Perennial	L
7	Fabales	*Medicago marina*	Garat	Th	Annual	H
8	Apiaceae	*Pituranthostortuosus*	Gezah	Ch	Perennial	H
9	Plantaginaceae	*Plantago lanculat*	Lisan alhmel	Ch	Perennial	H
10	Polygonaceae	*Polygoniumaviculare*	Grdab	Ch	Annual	M
11	Polygonaceae	*Polygonum equisetiforme*	Grdab	Ch	Perennial	H
12	Polygonaceae	*Thymelea hirsuta*	Methnan	Ch	Perennial	L

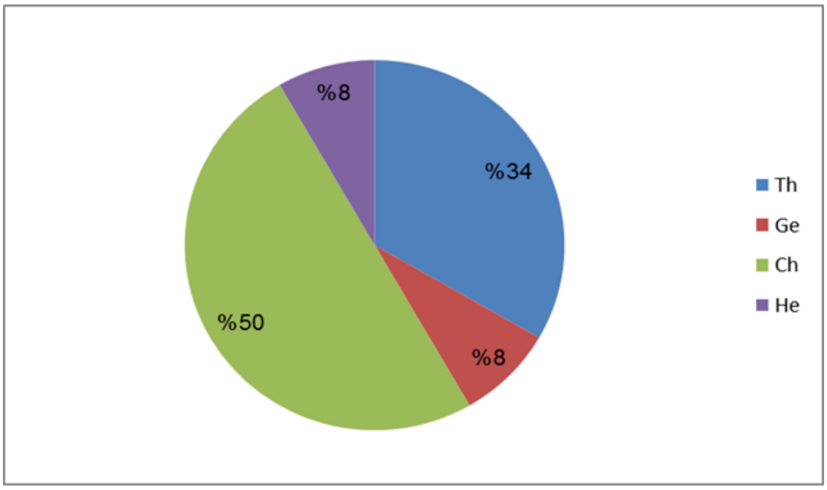

Fig.1. Life form of plant species collected from study area in In Al- briga Feild-Tobruk-libya.

Based on results, the most frequent plants belonged to Poaceae and **Polygonaceae** families According to the ability of some plants growing frequently in this area, one can conclude that these plants are useful for phytoremediation of those soils that are polluted with hydrocarbons and nickel. Gunther et al. (1995). ***Avena sterilis***, ***Cynodon dactylon***, ***Medicago marina***, ***Polygonum equisetiforme***, ***and Avena fatua*** It was the most frequentlly in studied locations(Appandix.1.). Various studies have reported the presence of some plants with high frequency in oil-contaminated areas (Mohsenzadeh et al. 2009; Chehregani Rad et al. 2014). Also, the results of current research indicated that survival of plants such as ***Polygonum equisetiforme***, ***Polygonium aviculare, Medicago marina***, and ***Pituranthos tortuosus*** was not inhibited by crude oil at the present concentrations. Regarding this, different studies have been accomplished to find native plants for phytoremediation purposes around the world (Bacchetta et al. 2015; Leguizamo et al. 2017). Our research indicated that some native species were resistant to petroleum pollution.

3.2. Total petroleum hydrocarbon distribution in planted and unplanted soil .

The concentrations of total petroleum hydrocarbons (TPH) in the planted soil and Unplanted soil show high concentration in Unplanted soil other Planted soil , the levels was location6 > location3 > location1> location 4> location 5 > location 2. The result of (TPH) in Planted soil was less than Unplanted soil ,it ranged between(3.36 and 5.76 **mg/kg^{-1} d.w**) (Table 2)(figer 2). There is strong significantly between TPH in Planted and Unplanted soil (P<0.001),and strong correlation between TPH in Planted and Unplanted soi (r=0.867). The result indicate that The concentration of TPH in planted area was 3.53±0.38 mg/kg^{-1} lower than its concentration in unplanted area (8.87±0.38 mg/kg^{-1} d.w). However, the location was found insignificantly influenced TPH concentration. The means separation showed that the significantly least concentration was recorded in the 2nd location while the greatest value was found in the 3rd location.

The pollution of Total Petroleum Hydrocarbon (TPH) is related to industrial activities that move into the environment and cause soil pollution. Contamination of soils with petroleum hydrocarbons is oneof the important environmental problems in some areas, particularly around petroleum refineries and fuel stations (Mosaed et al., 2015) .

Table 2: average concentration of TPH in planted and unplanted soil in selected sites

Location s	**plant species c**	**)TPH(mg/kg^{-1})**		***P***
		Plantedsoil	Unplantedsoil	
1	***Avena strerilis***	4.73	9.01	P<0.001
	Echium angustifolium	4.08	9.80	
2	***Erodium crassifolium***	4.33	7.30	P<0.001
	Malva sylvestris	-	7.80	
3	***Cynodon dactylon***	5.76	9.81	P<0.001
	Pituranthos tortuosus	3.76	9.84	
4	***Medicago marina***	4.76	8.71	P<0.001
	Plantago lanculat	3.36	8.80	
5	***Polygonium aviculare***	3.64	7.82	P<0.001
	Polygonum equisetiforme	3.53	7.79	
6	***Thymelea hirsuta***	-	9.80	P<0.001
	Avena fatua	4.41	9.84	

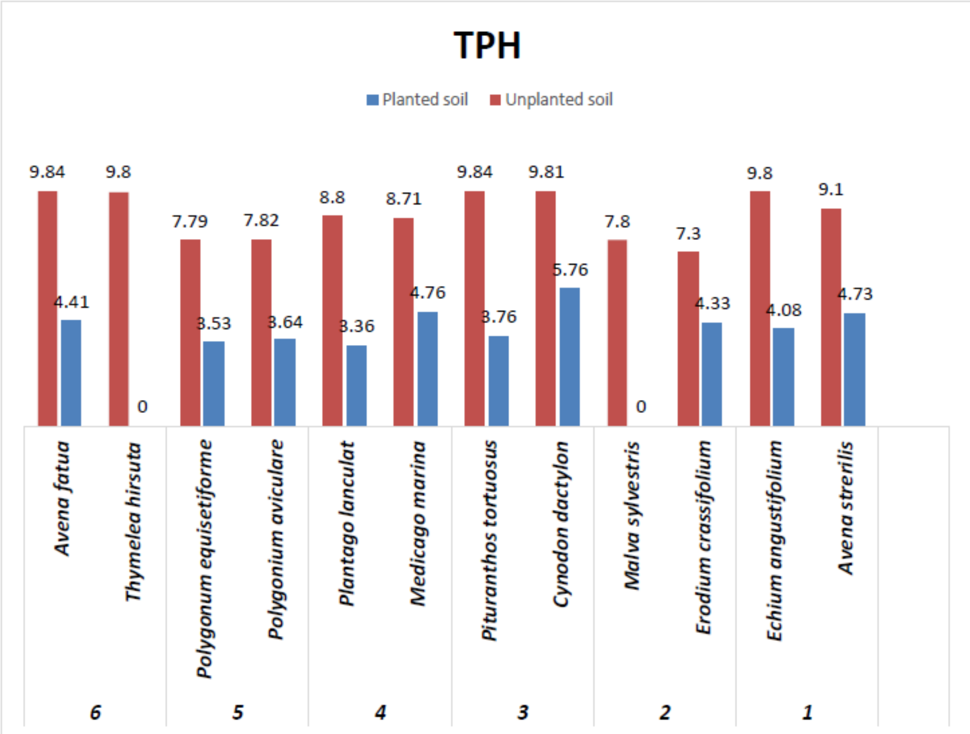

Fig.2. Average concentration of the TPH in planted and unplanted soil samples(mg/kg^{-1}d.w) collected from the studied locations.

3.2. Total petroleum hydrocarbon distribution in plant spesies

The result in (Table 3 and Fig.3) show variation in (TPH) between all studied plant species parts (root , and Shoot) , the high concentration found in *Medicago marina* root in location 4 (98.2 mg/kg^{-1}d.w),and *Polygonum equisetiforme* root in location5 (97.4 mg/kg^{-1}d.w)Comparison to other locations this level was highest than shoot of the plant in the same location as well as in the other locations. While in shoot the concentration was found higher in *Echium angustifolium* in location 1 (32.4) mg/kg^{-1}d.w,than *Erodium crassifolium* in location 2(25.2) mg/kg^{-1}d.w, compared with other locations. The concentrations of TPH in root samples in all of the studied plant species were higher than the planted soil levels. Showing that the root have higher ability to uptake the (TPH) from the soil compare with shoot samples. The concentration of TPH in plant root samples was observed in the order: *Medicago marina* > *Polygonum equisetiforme*> *Pituranthos tortuosus*> *Polygonium aviculare*> *Plantago lanculat*> *Echium angustifolium*> *Avena strerilis*> *Cynodon dactylon* > *Avena fatua*> *Erodium crassifolium* . There were positive correlation (r=0.93) between petroleum hydrocarbons in planted soil and studied plant spesies indicated that the plant spesies attained the TPH from the soil. The comparison of TPH content in the studied plant spesies samples shows that there is a higher uptake of TPH through root in mostof the studied plant species.. Higher concentration of TPH in the root than in the shoot samples showing more petroleum hydrocarbon pollution in the soil and transported to plant parts. The results of the study indicate the pollution of plant with petroleum hydrocarbon especially from soil which polluted by oil industry and from air polluted 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). so the mean of TPH concentration in root , and shoot compared with the mean concentration of planted soil in all studied locations . The levels was higher in root and shoot (98.2 , 43.6) mg/kg^{-1} d.w respectively than in planted soil 5.76 mg/kg^{-1} d.w. The mean of TPH in this study was higher 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 (shoot). TPH concentration in the root samples ranged between 20.1- 98.2 mg/kg^{-1} d.w.. 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 studied plant spesies and planted and unplanted soil was less than Permissible limit. The roots of studied plant spesies having more ability uptake of petroleum hydrocarbons through phytostabilization and,rhizidegradation mechanism. Phytostanilisation immobilize pollutants 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 pollutants 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 plantsor from soil organisms such as bacteria, yeast, and fungi. The lower concentration of TPH in shoot samples may have been caused due to phytodegradation or phyto transformation of petroleum hydrocarbons which was exposed the pollutants to the bioremedial processes occurring within the areal part of plant itself (Lotfinasabasl et al., 2013).

Table 3: average content of TPH in roots and shoots plants grown in the selectedsites.

Locations	plant species	)TPH(mg/kg^{-1} d.w)	
		Root	Shoot
1	***Avena strerilis***	28.2	20.8
	Echium angustifolium	29.7	32.4
2	***Erodium crassifolium***	20.1	25.2
	Malva sylvestris	n.d	n.d
3	***Cynodon dactylon***	28.1	20.8
	Pituranthos tortuosus	78.1	24.3
4	***Medicago marina***	98.2	43.1
	Plantago lanculat	68.2	32.7
5	***Polygonium aviculare***	75.7	21.6
	Polygonum equisetiforme	97.4	43.6
6	***Thymelea hirsuta***	n.d	n.d
	Avena fatua	21.5	20.4

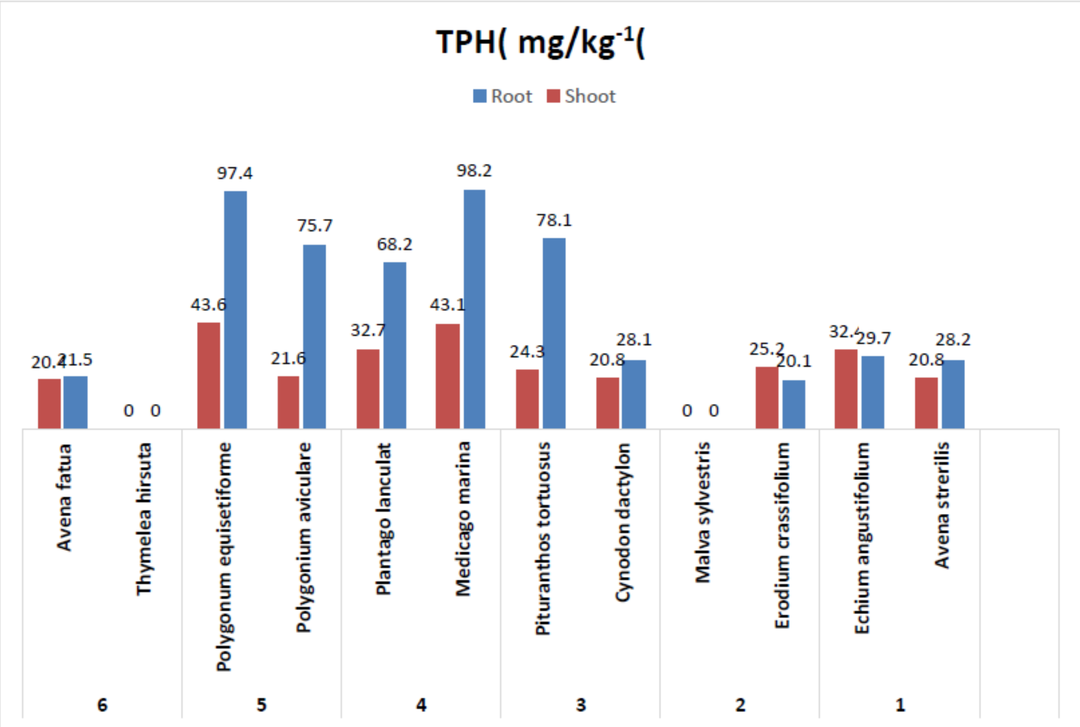

Fig.3. Average concentration of the TPH in root and shoot in plant samples (mg/kg^{-1}d.w) collected from the studied locations.

3.3. Bioconcentration and Translocation factors

The bioconcentration factor (BCF) and Translocation factor (TF) is very important factors to check the ability of plant spesies for phytoremediation (Al-Yameni et al., 2010) or to define the amount 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(4) show (BCF) and (TF) value.

Table4:The (BCF) and (TF)values of TPH in plant samples at studied locations.

Locations	plant species	BCF Root	TFshoot
1	*Avena strerilis*	1.82	0.37
	Echium angustifolium	0.56	1
2	*Erodium crassifolium*	0.34	1.25
	Malva sylvestris	0	0
3	*Cynodon dactylon*	2.38	0.74
	Pituranthos tortuosus	1.23	0.31
4	*Medicago marina*	1.44	440.
	Plantago lanculat	1.41	0.48
5	*Polygonium aviculare*	1.15	0.90
	Polygonumequisetiforme	1.00	0.45
6	*Thymelea hirsuta*	0	0
	Avena fatua	1.75	0.95

As in Table (6) There are high value of BCF in ***Cynodon dactylon*** root in location 3 and TF in ***Erodium crassifolium*** shoot in location 2 , while in locations 2,and 6 there is low BCF and TF value. in some studied plant spesies in studied locations the low BCF value was in roots 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 BCF in the present study indicates that the most studied plant spesies can tolerate high levels of petroleum hydrocarbons . the Bioaccumulation factor is known to decrease with increasing metal concentration in the soil , so the Plant spesies that growing at the situations 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 restricted ability of petroleum hydrocarbons accumulation and translocation by the plants (Nazir et al 2013). Then inthe present study the relationship between petroleum hydrocarbons concentration in planted soil and its concentration in studied plant spesiest show there are high capacity (positive correlation r=0.9 3) to accumulate pollutants in plant parts higher than in planted soil and Low TF in plant shoots , which can decrease with the increase of petroleum hydrocarbons in planted soil. Lotfinasabasl et al., 2013 ; whereas the lower TF value of the shoot samples demonstrates the uptake of hydrophilic petroleum hydrocarbons by the root and transfer to the leaf through vascular system, the greater BCF factor for the root indicates that phytoremediation. Chemicals that are highly water-soluble typically are not sufficiently sorbet to roots oractively transported through plant membranes, whereas hydrophobic chemicals, which are not water-soluble or are strongly bound to the surface of the roots and may not pass beyond the surface due to the high proportion of lipids present at the surface, cannot be easily translocated into the plant. (Lotfinasabasl et al., 2013) . Adesuyi et al.,(2015) reported that a higher Bioconcentration Factor value greater than one for plants (Croton lobatus, Borreria sp., Cyathula prostrata, Lantana camara, Ficus sp., Mimosa pudica, Eclipta prostrata, Commelina sp) wherase had limited ability to accumulate, translocate, and phytoextract. As an end result One of the significant environmental issues in some locations is the contamination of soil with petroleum hydrocarbons. In this study the concentrations of total petroleum hydrocarbons in planted and unplanted soil and plant parts (root and shoot) of studied plant spesies , which was concentrations in plant parts is higher than concentrations in planted and unplanted soil. The bioconcentration factor (BCF) estimated and the value< 1 was in most studied plant speies in all locations.

In conclusion, result from the study showed that the level of TPH in the studied plant roots was much higher than the level of TPH in the planted soil. Furthermore, the soils with the plants had appreciable lower level of TPH than the soil without plant. This is an indication that the most studied plants have potentials to remediate crude oil polluted soil. Also, from the result, it can be deduced that of the ***Avena strerilis***, ***Cynodon dactylon***, ***Pituranthos tortuosus***, ***Medicago marina, Plantago lanculat*** , ***Polygonium aviculare*** , ***Polygonum equisetiforme*** , ***Avena fatua*** has the greatest potential to remediate crude oil polluted soil.

IV. Conclusion

Based on the present study, it can be concluded that the native species ***Avena strerilis***, ***Cynodon dactylon***, ***Pituranthos tortuosus***, ***Medicago marina, Plantago lanculat*** , ***Polygonium aviculare*** , ***Polygonum equisetiforme*** ,**and *Avena fatua*** possess relevant characteristics for phytostabilization projects: they are tolerant to high levels of TPH contamination and are able to restrict TPH accumulation to root tissues, which in turn limits the risk of metals entering the food chain.

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Appandix.1. Number of species in studied locations.

Species	Locations						Total
	1	**2**	**3**	**4**	**5**	**6**	
Avena strerilis	**20**	-	**1**	-	**2**	-	**23**
Echium angustifolium	**11**	**2**	-	-	**1**	**3**	**17**
Erodium crassifolium	-	**10**	-	-	-	-	**10**
Malva sylvestris	-	**5**	-	-	-	**1**	**6**
Cynodon dactylon	**2**	**1**	**18**	**2**	**3**	-	**26**
Pituranthos tortuosus	**1**	-	**17**	**1**	-	**2**	**21**
Medicago marina	**1**	-	**4**	**19**	**1**	-	**25**
Plantago lanculat	-	-	**3**	**17**	**2**	-	**22**
Polygonium aviculare	**1**	**1**	-	**1**	**10**	**1**	**14**
Polygonum equisetiforme	**2**	-	-	**1**	**22**	**2**	**27**
Thymelea hirsuta	-	-	**1**	-	**2**	**4**	**7**
Avena fatua	**3**	**2**	-	**3**	**3**	**23**	**34**
Total	**41**	**21**	**44**	**44**	**46**	**36**	**232**