# EVALUATION OF SOME ORGANIC REMEDIES EFFECTS ON SOME SOIL PROPERTIES AND CROP

Esmaeil, M. A.; H. M. Khalil and S. H. Abd Elghany. Soils, Water and Environ. Res. Inst., Agric. Res. Center, Giza, Egypt.



#### **ABSTRACT**

This work aims to study the effect of contaminated soil remediation on some soil properties. Also a remediation experiment was conducted to show the useful effect of two remedies named Triton x-100 and potassium oleate in decreasing the hydrocarbons (aliphatic and aromatic) and heavy metals contents in crude oil contaminated soil samples. Two soils (sandy and calcareous) were contaminated by 1 , 2 and 3 % V/W of crude oil, then each contamination level was treated by 0 (untreated), 1 and 3 % of the two used remedies. Pots were seeded with barley seeds, barley plant samples were collected at the end of the experiment. The total concentrations of nitrogen, phosphorus and potassium in plant samples and soil under study were estimated. Also, the concentration of hydrocarbons and heavy metals were measured. It can be deduced from the data obtained from this study that the total contents of nitrogen, phosphorus and potassium were significantly affected by contamination by crude oil. Application of Triton x-100 and potassium oleate decreased to high extents the concentrations of aliphatic and aromatic hydrocarbons as well as the heavy metals. For example, the use of Triton x-100 reduced the concentration of aliphatic hydrocarbons by percents reached to 54 % as compared to the non-remedied samples. On the other hand, the concentration of heavy metals as Nickel also decreased by about 55 %, which confirms the efficiency of the used remedies. Also, application of these remedies had increased the total contents of organic carbon, nitrogen, phosphorus and potassium in the treated samples than those in untreated ones. The application of organic remediation of contaminated soils led to limited increase on EC and pH values this result confirms the importance of these organic remedies to reduce the harmful effects on the properties of remedied

#### INTRODUCTION

There are big amounts of pollutants which contaminate the environment especially the soils arise from civilized development and industrial progress. As a result, pollution remediation and cultivated soil protection are very important two challenges that meet us in the 21<sup>st</sup> century. In Egypt, most of the industrial factories lie beside or near from cultivated soils. One of the most serious sources is the pollution by petroleum hydrocarbons arising from crude oil. Contamination by crude oil components can cause severe and lasting damage if it is accidentally discharged into water or soil. Petroleum hydrocarbons concentrations in oil polluted sediments that more than 100 µg/g give an indicator for a heavy polluted soil (Marchand *et al.,* 1982). The levels of total polycyclic aromatic hydrocarbons (PAHs) in River Nile water ranged from 1112.7 to 4351.2 ng.I<sup>-1</sup>. Some PAHs and their epoxides are highly toxic, it is significant that the mean values of the total PAHs found in water samples collected from four sites along the River

Nile were among the highest values recorded in other world areas (Badawy and Embaby, 2010).

The analyses obtained by gas chromatography revealed that the main hydrocarbons in the contaminated soils were n-paraffins with n (number of carbon atoms) ranged between 12 and 30 carbon atoms. Total contents of some heavy metals (Cd, Pb, Zn, Cu, Fe and Mn) were evaluated in soil contaminated with crude oil of oil well at Ras-Sudr. The average concentrations for these heavy metals were 6.9 , 63.0 , 120.0 , 22.6 , 8563 and 649.0  $\mu$ g/g for Cd, Pb, Zn, Cu, Fe and Mn, respectively (Ismail, 2000).

Crude Oil contamination can affect soil physical and chemical properties. Oil usually causes anaerobic environment in soil by smothering soil particles and blocking air diffusion in the soil pores, and affects soil microbial communities (Sutton *et al.*, 2013). Heavy crude oil pollution can cause complete mortality of marsh vegetation (Lin and Mendelssohn, 2012). Hydrocarbon contamination can also increase soil total organic carbon (Ekundayo and Obuekwe, 2000), and change soil pH values (Wang *et al.*, 2010) and other soil chemical properties (Kisic *et al.*, 2009). Crude oil contamination significantly increases the soil pH up to 8.0, and reduces available phosphorus concentrations in the soil. Therefore, crude oil contamination could potentially alkalinize soils, adversely affect soil fertility and physical properties, Crude oil contamination affects the soil physical and chemical properties, so must be developing an fertility restoration program in the contaminated soils (Wang *et al.*, 2013).

Barley (Hordeum vulgare) is a fast growing, cool season, annual grain crop that can be used as forage or as a cover crop to improve soil quality. It is well known that nitrogen simulates root growth and uptake of nutrients whereas phosphorus is essential for metabolic processes and potassium balances the nutrient uptake by plants (Kshirsagal and Aery, 2007). Leo and Iruka (2007) affirmed that such high hydrocarbon levels affect both above-ground and subterranean flora and fauna, which are essential adjuncts in the biogeochemical cycle that affects availability of plant nutrients. In general, plants require 16 essential elements for growth, 13 come from the soil, three of which (N, P, and K). The concentrations of extractable macronutrients N, P and K in the oil-impacted area were significantly lower than in adjacent control plots. The introduction of degradable hydrocarbon has altered the carbon to nutrient ratio well beyond recommended for balanced soil nutrition. The C: N, C: P and C: K ratios can be adjusted with the application of additional inorganic N, P and K fertilizers. Oil reduces soil fertility such that most of the essential nutrients are no longer available for plant and crop utilization (Abii and Nwosu, 2009).

#### Remediation of hydrocarbons and heavy metals contaminated soils:

The hydrocarbons found in crude-oil spillage are large and complex molecules, and persistent in nature and may require a strong reagent to counteract their effects on agricultural soil (Whitten *et al.*, 1985). The process of crude oil clean up on land has been extensively researched upon (Holliday and Deuel, 1993). Remediation processes like, land farming, soil washing,

vapour extraction, thermal desorption, composting and many others are either expensive or not environmentally sound.

Petroleum hydrocarbons (PHCs) usually consist of alkanes (linear or branched), cycloalkanes, aromatic hydrocarbons or more complex chemicals (Pernar et al., 2006). There are three main approaches in dealing with contaminated sites: identification of the problem, assessment of the nature and degree of the hazard, and the best choice of remedial action. The need to remediate these sites has led to the development of new technologies that emphasize the detoxification and destruction of the contaminants (Wang, 2007). The remediation of PHCs contaminated soils has attracted world wide attention (Euliss et al., 2008). In comparison with conventional ex situ methods, such as incineration, off-site storage, soil washing and in situ capping for stabilization, in situ phytoremediation as a polishing green technology that uses higher plants to degrade, transform, assimilate, metabolize, or detoxify hazardous pollutants from environments has a lot of advantages (Chaudhry et al, 2005). Plants growing on these soils show a reduction in growth, performance, and yield. Bioremediation is an effective method of treating heavy metal polluted soils (Chibuike and Obiora 2014).

Remediation processes like, Land farming, soil washing, vapors extraction, thermal desorption, composting and many others are either expensive or not environmentally sound. Ismail (2000) found that using organic remedies and inorganic as bentonite (clay mineral) was very useful in remediation of soil contaminated with petroleum hydrocarbons of crude oil at Ras-Sudr. Pena *et al.* (2011) used Sodium Dodecyl Sulfate (SDS) as anionic surfactant and Tween 80 as nonionic surfactant to remediate dimethoate to recover this pollutant and prevent it from penetration to ground water and pollute it.

Laboratory column experiments were conducted to investigate the performance of anionic-nonionic mixed surfactant, Sodium Dodecyl Sulfate (SDS) with Triton X-100 (TX100), in enhancing phenanthrene flushing for contaminated soil in an aim to improve the efficiency of surfactant remediation technology. The experimental results showed that the sorption of TX100 onto soil was severely restricted in the presence of SDS in batch and column experiments and decreased with the increasing mass fraction of SDS in mixed surfactant solutions; meanwhile the enhanced solubilization of phenanthrene by SDS-TX100 mixed surfactant was greater than that by individual surfactant. These results can be attributed to the formation of mixed surfactant micelles in solution (Wenjun and Lizhong 2008).

Mukhopadhyay *et al.*, (2012) studied the effect of soapnut and sodium dodecyl sulfate (SDS) on removal of Cadmium from contaminated soils. It was found that 2.5 % soapnut had the best removal effect of cadmium. It was observed that soapnut solution is successful in achieving up to 80% removal rate as that of SDS. Keeping in mind the fact that soapnut is biodegradable and can be left in-situ without any fear of toxicity and soil pollution.

Since oil pollution is a worldwide threat to the environment, hence the remediation of oil-contaminated soils, sediments and water is a major challenge for environmental research. Many studies have focused on the impact of crude oil on the physical and chemical properties of the soil contamination and the impact on the plant. This study is concerned to the effects of some organic remedies on some soil properties and crop.

#### **MATERIALS AND METHODS**

To investigate the effect of the two used remedies (Triton x-100 and Potassium Oleate), a pot experiment was carried out at Bahtim Experimental Research Station, Kalubia Governorate (Latitude 30° 8′ 31.316″ N and Longitude 31° 16′ 53.714″ E). Sandy and calcareous soils were contaminated by crude oil at 4 concentration levels: without oil (control), 1 %, 2 % and 3 % oil v/w (ml/kg). The used remedies were added to each contamination level by ratios: without remedy (control), 1 % and 3 % v/w. The experiment was conducted in the winter season 2013/2014 to evaluate some organic remedies effects on some soil properties, contaminants and crop. The chemical and physical properties of sandy and calcareous soils under study are illustrated in Table (1).

Chemical symbol of the Triton x-100 and Potassium Oleate under study are :-

- Triton x-100 = alkyl phenol ethoxilate = CH<sub>3</sub>-C (CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-C (CH<sub>3</sub>)<sub>2</sub>-φ-(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>X</sub> OH according to Wachs and Hayano, (1962).
- Potassium Oleate soap CH<sub>3</sub>-(CH<sub>2</sub>)<sub>7</sub> CH= CH-(CH<sub>2</sub>)<sub>7</sub> COOK according to Roch and Alexander, (1995).

The experiment was laid out in spilt-split plot design with three replications for each experiment unit. The main pots were two soils (sandy and calcareous), the sub-main were 4 crude oil contaminated levels (without remedy, 1, 2 and 3% crude oil) while sub sub-main were 5 organic remedies (without, 1 and 3% of the two remedies) in three replicates. The plastic pots of 20-cm diameter and 20-cm depth were filled with 2 Kg contaminated soil. Remedies were added once to the pots with first irrigation water at 100% of field capacity. Then the soils were leached by irrigation every 15 days for a period of five months until planting during the winter season. Nitrogen, phosphorus and potassium fertilizers were added to the pots at the recommended doses (60 kg N, 15 kg  $P_2O_5$  and 24 kg  $K_2O$  fed<sup>-1</sup>). These Nitrogen, phosphorus and potassium fertilizers were added in the forms of ammonium nitrate (33.5 % N), superphosphate (15.5 %  $P_2O_5$ ) and potassium sulfate (48 %  $K_2O$ ), respectively. The pots were then cultivated by barley seeds (*Hordeum vulgare* L., cv. Giza 123).

Surface soil samples (0-30 cm layer) were collected from each pot after harvesting, and then dried, grounded and subjected to determine available nutrients of N, P and K as outlined by Black (1983). Available heavy metals concentrations (Pb, Cd and Ni) were estimated according to Soltanpour and Schwab (1977). Soil pH was measured according to Thomas (1996), whereas electrical conductivity (EC) was measured according to Rhoades (1996).

Table (1):Some physical and chemical properties of the experimental soils

experime	iitai 50ii5					
	Soil	characte	ristics			
Particle size distribut	ion %		Cations	xtract		
	Soil (1)	Soil (2)	Loamy	y sand	Soil (1)	Soil (2)
Sand	87.19	41.56	satur		20.8	47.9
Silt	1.99	26.72		a <sup>++</sup>	9.98	22.1
Clay	10.82	31.81	Mg	g <sup>++</sup>	7.93	15.54
Texture class	Loamy sand	Clay loam	N	a <sup>†</sup>	11.95	25.66
CaCO₃%	6.46	K	(+	1.99	3.35	
OM%	0.8	1.45	.45 CO <sub>3</sub>			-
CEC meq 100 <sup>-1</sup> g	9.21	27.2	HC	O <sub>3</sub> -	7.89	12.2
pH(1:2.5 soil suspension)	7.42	7.95	С	L <sup>-</sup>	10.2	31
EC dS/m (in pest extract)	1.8	5.82	SC	D <sub>4</sub>	13.76	23.45
Available	N soil (1)	N soil (2)	P soil (1)	P soil (2)	K soil (1)	K soil (2)
macronutrients (mg kg <sup>-1</sup> )	33	24	16 12		61	52

Soil (1) =sandy soil soil (2) = calcareous sail

Plant samples of barley were collected from pots after 45 days, weighed, oven dried at 70  $^{\circ}$ C, grounded and prepared for digestion using H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> as described by page *et al.* (1982). The digests were then subjected to measurement for macronutrients (N, P and K) using the procedure described by Ryan *et al.* (1996).

The crude oil obtained from the pipe line company of Tanta was analyzed by Gas Chromatography (GC) to estimate its components. Hydrocarbons were extracted from soil samples through two stages including extraction, then clean up and separation, and then analyzed by Gas Chromatography (US-EPA, 1997 and UNEP/IOC/IAEA, 1992).

All data were subjected to statistical analysis of variance and treatment means were compared using Costat computer package to calculate F ratio according to the Least Significant Differences (L.S.D.) test method as described by SAS Institute (1985).

## **RESULTS AND DISCUSSION**

Effect of using remedies of contaminated soil on the dry matter yield and NPK uptake of barley plant:

In this experiment, after the addition of remedies into the soil and washing for six months by repeating the irrigation every 15 days, the soil was cultivated by barley seeds to study the effect of these remedies on crops dry

matter and inorganic nutrients uptake, as well as the content of elements in the soil. As shown in Table (2), it can be concluded that there was a positive impact of remedies on the dry matter (g/pot) and NPK uptake (mg/pot) of barley plant during the treatment period. The mean values in soils without remedy were 0.83 g/pot dry matter, 2.27, 0.53 and 2.11 mg/pot N, P and K uptake by barley (these values are lower than that in the remedied soils). Also, the dry matter g/pot and NPK uptake obtained with Triton X-100 at 1 and 3 % remediation levels were better than those in soils treated with potassium oleate. These results confirm the superiority of Triton X-100 to remove crude oil components from the soil. The relationships between NPK elements and growth or dry matter production of common buckwheat were investigated. Phosphorus deficit affected the growth, yield and NPK elements uptake. Nitrogen and phosphorus affected more seriously on dry matter production than on plant growth. On the other hand, potassium affected growth characteristics but did not affect yield characteristics (Hisayoshi, 2001). On the other hand, organic and inorganic fertilizer enhances the growth in a crude oil polluted soil. There was a general improvement in the growth, dry weight, chlorophyll content, leaf area and pod production of the crop by the addition of cow dung to crude oil polluted soil. The performance of the crop also improved as the period of study increased suggesting that the toxicity of crude oil to the crop reduced as the period of study increased (Kelechi, et al., 2008).

On the other hand, the dry matter and NPK uptake of barley grown in sandy soil was significantly increased than in calcareous soil. The mean value was 1.36 g/pot dry weight and 3.03, 0.65 and 2.72 mg/pot for N, P and K uptake by barley in sandy soil comparing by 1.27 g/pot dry weight, 2.36, 0.53 and 2.05 mg/pot N, P and K uptake by barley in calcareous soil, respectively. This result may return to the appropriate physical properties of sandy soil than that of the calcareous soil after the washing process. Frequently, calcareous soils are associated with plant nutritional problems such as micronutrient deficiencies and low phosphate availability (formation of unavailable calcium phosphate). These constraints to plant growth are often compounded by restrictive soil physical properties including the formation of surface crusts, shallow depth, high stone contents and, low plant available water, especially in dry regions or during extended dry seasons (Ian Grange, 2001).

Table (2): Dry matter yield of barley plant and (NPK) uptake as affected by type, concentration and remedies of soil contaminated by crude oil

Soil		Dry matt		pla	ant		N uptake (mg/pot) in bariey							
contaminated by crude oil %		Тур		d Co ton		nedies		Type and Con. Remedies (A						
		Without Remedy	x-100		•	ΛΙΔ2ΤΔ		Without Remedy	v-100		oleate		Mean (B)	
		Keilleuy	1 %	3%	1 %	3%	(B)	Keilleuy	1 %	3%	1 %	3%	(0)	
	0%	1.15	2.12	2.55	1.60	2.12	1.91	3.40	3.76	4.39	3.10	3.85	3.70	
nd ie	1%	0.80	1.50	2.03	1.14	1.70	1.43	2.43	3.30	4.02	2.92	3.40	3.21	
Sandy soil	2%	0.78	1.04	1.83	1.02	1.47	1.23	1.95	2.81	3.48	2.69	2.94	2.77	
٥٫	3%	0.52	0.90	1.35	0.83	1.16	0.95	1.80	2.68	3.20	2.40	2.62	2.54	

	Mean	0.81	1.19	1.94	1.15	1.61		2.40	2.89	3.77	2.78	3.20	
Soil (	C )						1.36						3.03
<b>(0</b>	0%	1.40	1.75	1.98	1.50	1.74	1.67	2.64	2.80	3.20	2.86	2.97	2.89
Calcareous soil	1%	0.71	1.34	1.70	1.24	1.51	1.30	2.30	2.47	2.95	2.51	2.60	2.57
soil	2%	0.69	1.22	1.56	1.20	1.42	1.22	1.93	2.10	2.21	1.98	2.08	2.06
Salc	3%	0.62	0.96	1.20	0.76	0.96	0.90	1.72	1.99	2.08	1.90	1.98	1.93
O	Mean	0.86	1.32	1.61	1.18	1.41		2.15	2.34	2.61	2.31	2.41	
Con. mean	Remedies (A)	0.83	1.25	1.77	1.16	1.51		2.27	2.61	3.19	2.54	2.80	
Soil (	C )						1.27						2.36
LSD 1	% =	A=0.0	)4***	B=0.	04***	C=0.06	**	A=0.0	21***	B=0.0	)22*** (	C=0.026	5***
		Р	uptak	e (mg/	/pot) in	barley		K					
	0%	0.71	0.75	0.83	0.77	0.84	0.78	4.03	4.30	4.51	4.14	4.20	4.24
<u></u> ≈ _	1%	0.66	0.70	0.77	0.69	0.74	0.71	2.37	2.70	2.96	2.60	2.78	2.68
Sandy soil	2%	0.53	0.58	0.67	0.55	0.60	0.59	2.15	2.31	2.35	2.16	2.20	2.23
S.	3%	0.48	0.53	0.61	0.50	0.55	0.53	1.50	1.72	1.83	1.64	1.90	1.72
	Mean (B)	0.60	0.64	0.72	0.63	0.68		2.51	2.76	2.91	2.64	2.77	
Soil (	C )						0.65						2.72
S	0%	0.68	0.71	0.76	0.69	0.72	0.71	2.97	3.32	3.51	3.04	3.20	3.21
noe_	1%	0.53	0.65	0.70	0.59	0.62	0.62	2.00	2.51	2.80	2.28	2.34	2.39
Calcareous soil	2%	0.34	0.50	0.58	0.40	0.42	0.45	1.14	1.60	2.00	1.43	1.55	1.54
Salc	3%	0.28	0.39	0.44	0.33	0.36	0.36	0.75	1.16	1.30	0.87	1.17	1.05
O	Mean (A)	0.46	0.56	0.62	0.50	0.53		1.72	2.15	2.40	1.91	2.07	
Con.R means	Remedies s	0.53	0.60	0.67	0.56	0.60		2.11	2.46	2.66	2.28	2.42	
Soil (	C)	•			•		0.53						2.05
LSD 1	%	A=0.0	10***	B=0.0	)10*** C	C=0.014	***	A=0.1	05***	B = 0.1	02*** C	C=0.142	***

(A)=Type and Concentration of Remedies, B=concentration of crude oil %, C=soil, N=nitrogen, P=phosphate, K=potassium

Data in Table (2) illustrate also the impact of using remedies on dry matter yield of barley in the presence of soil contamination levels of 0, 1, 2 and 3%. It can be deduced that using remedies improved dry matter yield and NPK uptake of barley plant. Results also suggested increasing the efficiency of remedies with the increase of application rate of remedies in the contaminated soils. Perhaps likely that the success of organic remedies in the removal of the negative impact of oil pollution. Spilled crude-oil which is denser than water reduces and restricts permeability: organic hydrocarbons which fill the soil pores expel water and air, thus depriving the plant roots the much needed water and air (Brian, 1977). 3% concentration crude oil has been reported to be increasingly deleterious to soil biota and crop growth (Osuji et al., 2005). Soil properties involved in soil-plant-water relationship as texture, infiltration, hydraulic conductivity, moisture content, pH and density affect root and leaf development and plant growth and yield (Michael and Ojha, 2006).

# Effect of using remedies on concentrations of the contaminants in the treated soils:

It is necessary to use proper remedies to decrease concentrations of hydrocarbons and heavy metals from the soil and improve its chemical and physical properties. Data presented in Table (3) show effect of using Triton x-100 and potassium oleate on total petroleum hydrocarbons (TPH), aliphatic and aromatic contents as well as cadmium, lead and nickel in sandy and calcareous soils that contaminated by different concentrations of crude oil.

Data indicate that Triton x-100 was more effective and more significance as a remedy than potassium oleate after remediation process. The lowest values were 287 and 250 ppm for TPH, 181 and 154 ppm for aliphatic and 106 and 95 ppm for aromatic hydrocarbons at remedy rate 1 % and 3 % Triton x-100, respectively. Also lowest values of heavy metals were 0.13 and 0.11 ( $\mu$ g/g Cd), 1.48 and 1.24 ( $\mu$ g/g Ni) and 3.87 and 3.28 ( $\mu$ g/g Pb) at remedy rate 1 % and 3 % Triton x-100, respectively. This result is compatible with the results of Ismail, (2000).

Also, TPH or aliphatic and aromatic hydrocarbons as well as heavy metals contents significantly decreased in sandy soil by a rate more than that in calcareous soil. The lowest values were 279, 178 and 99.6 ppm for TPH, aliphatic and aromatic hydrocarbons, respectively. While heavy metals values were 0.121, 3.31 and 1.36  $\mu$ g/g for Cd, Pb and Ni in sandy soil, respectively. Conversely, the higher values of such components were found in calcareous soil that were 334, 216 and 117 ppm for TPH, aliphatic and aromatic as well as heavy metals values which were 0.148, 4.35 and 1.70  $\mu$ g/g (Cd, Pb and Ni). Apparently, TPH, aliphatic, aromatic and heavy metals Cd, Ni and Pb values in remedied soil were lower than those in soil before remedy.

## Effect of remediation on some contaminated soil properties:

Data in Table (4) represent the effect of the applied levels of remedies on some soil properties, i.e., pH, EC, OM and availability of NPK in the remediated soil after barley harvest. Concerning pH values, results show that remedy application generally, significantly increased pH values as compared to without remedy. Also, the gradual increase of pH values was related to the increase of soil contamination levels. Also, the increase in pH values in calcareous soil was higher than those in sandy soils. These results may be due to the moderate alkaline soil in this study, with the presence of some interactions that may increase the OH ions. Clean contaminated soil by using chemical degraders and detergents affect soil properties and crop growth; however, soil pH increased by 5 %. These may be attributed to bacterial biodegradation of crude oil under the anaerobic conditions present in the soil macro and micro-pores (Essien and John, 2010). Variations in soil properties can affect the rates and extents of chemical loss (Rhodes et al., 2008) whereby the composition of a soil's mineral and organic matter fractions may enhance or retard the loss of the HOCs (Semple et al., 2003).

Table (3):Efficiency of remedies type and concentration on TPH, aliphatic, aromatic and some heavy metals contents of soil contaminated by crude oil.

	,	Jonitani	ma	<del>c</del> u	Oy Ci										
	Call		T	PH (	(ppm)	·		Aliphatic hydrocarbons							
Soil contaminated by cured oil %		Тур	e an	d Co	n. Re	medie	s	Type and Con. Remedies (A)							
		Without Remedy	Triton x-100		potassium oleate		Mean (B)	Without Remedy	Triton x-100		potassium oleate		Mean (B)		
	70	Remeuy	1 %	3%	1 %	3%	(6)	Keilleuy	1 %	3%	1 %	3%			
	0%	7.66	5.00	5.55	6.00	6.00	5.93	4.33	2.00	2.00	3.00	3.00	2.86		
<b>≳</b> _	1%	349	220	177	255	218	243	231	136	106	161	143	155		
Sandy soil	2%	479	323	280	370	337	357	311	199	171	230	221	226		
	3%	641	479	406	535	496	511	426	307	251	345	324	330		
	Mean	369	256	217	291	264		243	161	132	184	172			

S	Soil ( C )						279						178
	0%	6.00	5.00	5.00	6.00	5.33	5.46	4.00	3.00	3.00	3.33	3.00	3.26
snc	1%	300	261	228	296	262	269	253	167	142	192	177	186
Calcareous soil	2%	528	403	366	442	408	429	342	246	222	280	267	271
alc	3%	714	607	538	638	593	618	475	389	342	423	404	406
0	Mean	387	319	284	345	317		268	201	177	224	212	
Con.	Remedies	388	287	250	318	290		255	181	154	204	192	
	nean (A)	300	201	250	310	290		255	101	154	204	192	
	Soil (C)						334						216
LS	SD 1 % =					=0.43*	**	A	=0.09		=0.10**		28***
					droca						d (µg/g		
	0%	3.00		3.00		3.00	3.00	0.04		0.04		0.04	0.039
중_	1%	118	84	71	93	75	88.2	0.13		0.08	0.11	0.10	0.104
Sandy soil	2%	168	124	109	139	116	131	0.19		0.12	0.17	0.12	0.152
တ	3%	215	172	155	166	172	176	0.24		0.16	0.20	0.18	0.192
	Mean (B)	126	95	84	100	91		0.15	0.12	0.09	0.13	0.11	
S	Soil (C)						99.6						0.121
<u>s</u>	0%	2.33		2.33	2.66	2.33	2.40	0.07	0.05		0.06	0.06	0.056
Calcareous soil	1%	127	94	86	104	85	99.2	0.16	0.12		0.14	0.13	0.132
care	2%	186	157	144	162	142	158	0.21	0.17		0.19	0.18	0.180
Cal	3%	240	218	196	216	189	211	0.27	0.22		0.24	0.20	0.225
	Mean (A)	138	117	107	121	104		0.17	0.14	0.12	0.15	0.14	
	Remedies	132	106	95	110	98		0.16	0.13	0.11	0.14	0.12	
	means												0.440
	Soil ( C ) SD 1 %	۸ 1	.89**	D F (	>F*** O	40.5*	117	A=0	0.148				
	SD 1 %	A=4	.89""			=12.5*		A=0	.002***				
	0%	0.70	0.50	<b>Ni (μ</b> 0.32		0.54	0.52	2.14	1.62	1.51	o (μg/g) 2.01		1.82
	1%	0.70 1.48	0.50 1.16	1.07	0.62 1.14	1.02	0.53 1.17	3.1		2.15	3.078	1.82 2.66	2.82
ق≅	2%	2.01	1.10	1.07	1.14	1.02	1.17	4.49	4.14		3.078	2.80	3.52
Sandy soil	3%	2.72	2.18	1.52	2.45	2.28	2.23	6.12		4.25	5.32	4.86	5.11
"	Mean (B)	1.72	1.31	1.03	1.45	1.28	2.23	3.96		2.70	3.41	3.03	3.11
	Soil ( C )	1.72	1.51	1.03	1.43	1.20	1.36	3.30	5.41	2.70	3.41	3.03	3.31
	0%	0.96	0.64	0.58	0.79	0.66	0.72	2.26	1.82	1.60	1.90	1.78	1.87
sno	1%	1.72		1.26	1.64	1.43	1.49	4.12		3.12	4.02	3.61	3.72
soil	2%	2.58	2.03		2.30	1.92	2.11	6.18	5.26	4.72	5.83	4.31	5.26
Calcareous soil	3%	3.08	2.50		2.48	2.17	2.50	7.74		6.01	6.92	5.83	6.58
Ö	Mean (A)	2.08	1.64	1.45	1.80	1.54	2.00	5.09	4.28	3.86	4.66	3.88	0.00
Con	Remedies												
	means	1.90	1.48	1.24	1.62	1.41		4.53	3.87	3.28	4.04	3.45	
	Soil ( C )				1	1	1.70				1		4.35
	SD 1 %	A=0.0	14***	B=0.0	)15*** (	C=0.03		A=0.014*** B=0.01*** C=0.025***					
LSD 1 % A=0.014*** B=0.015*** C=0.035*** A=0.014*** B=0.01*** C=0.025***  (A) = Type and Concentration Periodics Reconcentration cured oil % C = soil A*B*													

(A) = Type and Concentration. Remedies, B=concentration cured oil %, C = soil A\*B\*C =interaction analysis.

Regarding the EC values, data in Table (4) reveal that the application of remediation of soil contamination increased EC value. This increase was low for the use of organic remedies (Triton x-100 and Potassium Oleate) not containing sodium. The detergents are usually large chemical composition of sodium salt like sodium lauryl benzene sulfonate (Whitten *et al.*, 1985). This result confirms the importance of these organic remedies in reducing the harmful effect on the properties of contaminated soil. Also Triton x-100 had a less impact on the increase of salinity compared with Potassium Oleate. On the other hand, soil contamination has an effect on increasing its salinity. The increase in salinity of calcareous soil was higher than in sandy soil. This result confirmed ease remediation of sandy soil compared to calcareous soil.

Saline and hyper saline environments are frequently accompanied with crude oil contamination as a result of industrial activities. Soil salinization has great inhibitory effects on the biodegradation of petroleum hydrocarbons (Mille *et al.*, 1991).

The results show the positive and significant effect of the using of organic remediation on the content of organic matter, nitrogen, phosphate, potassium in sandy and calcareous soils after harvest.

Results in Table (4) indicate that application of Triton x-100 significantly increased OM, N, P and K contents higher than the increase resulted by using Potassium Oleate in soil. Also, the increase of OM, N, P and K values in calcareous soil was higher than OM, N, P and K in sandy soils. This result may be attributed to soil properties under study. Soil structure and physicochemical and biological characteristics, e.g., soil organic matter content, bulk density, porosity, permeability, soil respiration and material transfer process can be altered by the high hydrophobicity of hydrocarbons (Liang et al., 2012). On the other hand, the gradual decrease of OM, N, P and K values was related to the increase of soil contamination levels. With the importance of the results in this study to assess the type and concentration of the appropriate processor, but the application of two or more remediation techniques is necessary to improve the bioavailability and bioremediation with organic remediation efficiency considering the harsh contaminated environment.

Table(4): Efficiency of type and concentration of remedies on some characteristics of soil contaminated by crude oil.

	Onai							ted by						
		_				r harv		ECe (dS m <sup>-1</sup> ) in soil after harvest Type and Con. Remedies (A)						
Soil		Тур				medies	s	Туре					(A)	
	aminated	Without	Trito	n x-	potas	ssium	Maan	Without	Trito	n x-	potas	ssium	Mean	
by cu	ıred oil %	remedy	100		ole	ate	(B)	Remedy	100		oleate		(B)	
		remedy	1 %	3%	1%	3%	(D)	Keilleuy	1 %	3%	1 %	3%	(D)	
	0%	7.4	7.6	7.6	7.5	7.5	7.54	1.80	1.84	1.85	1.83	1.83	1.83	
	1%	7.5	7.6	7.6	7.7	7.8	7.64	2.00	2.45	2.49	2.27	2.30	2.30	
dy	2%	7.7	7.7	7.8	7.8	7.8	7.78	2.25	2.34	2.36	2.27	2.28	2.30	
Sandy soil	3%	7.8	7.9	7.9	7.9	7.9	7.89	2.40	2.51	2.53	2.47	2.51	2.48	
ຫ ທ	Mean	7.6	7.71	7.75	7.73	7.76		2.11	2.28	2.30	2.21	2.23		
Soil (	C)						7.71						2.22	
S	0%	7.9	8.0	8.0	8.0	8.0	7.99	5.82	5.90	5.93	5.88	5.90	5.88	
Calcareous soil	1%	8.2	8.2	8.2	8.3	8.3	8.26	6.53	6.62	6.68	7.01	7.13	6.79	
soil	2%	8.3	8.3	8.4	8.4	8.4	8.39	6.70		6.84	7.11	7.20	6.93	
Calc	3%	8.4	8.5	8.5	8.5	8.6	8.51	7.14	7.14	7.50	7.30	7.38	7.29	
	Mean	8.0	8.2	8.2	8.3	8.3		6.54	6.62	6.73	6.82	6.90		
	emedies	7.92	7.99	8.02	8.02	8.32		4.33	4 45	4.52	4.51	4.56		
mean		7.52	7.55	0.02	0.02	0.02		4.00	7.70	7.02	7.01	4.00		
Soil (							8.29						6.72	
LSD 1	% =	A=0.0				C=0.049	9***		069**			C=0.16'		
					after h			Availab						
	0%	0.80		0.85	0.81	0.82	0.82	22	23	23	22	23	22.6	
_	1%	0.91	0.95		0.91	0.94	0.93	19	20	21	20	20	20.0	
ng _	2%	1.01	1.04		1.02	1.03	1.03	16	19	19	20	21	19.0	
Sandy soil	3%	1.10	1.14	1.16	1.11	1.12	1.12	14	15	16	13	15	14.6	
	Mean (B)	0.95	0.99	1.01	0.96	0.97	0.00	17	19	19	18	19	40.0	
Soil (		4.40	4 4 4	4 40	4 40	1 40	0.98	40	47	47	40	40	19.0	
Sn	0%	1.40	1.44	1.46	1.43	1.46	1.43	16	17	17	16	16	16.4	
Calcareous soil	1% 2%	1.45	1.50	1.53	1.48	1.50	1.49	14 12	15 13	15 14	14 13	14 12	14.4	
SC	3%	1.63 1.72	1.69 1.78	1.71	1.64	1.66 1.82	1.66 1.78	8	10	11	10	10	12.8	
ပိ	Mean (A)	1.72	1.60	1.62	1.77	1.62	1.76	12	13	14	13	13	9.93	
Con B	emedies means	1.25	1.29	1.32	1.27	1.29	ł	15	16	17	16	16		
Soil (		1.23	1.29	1.32	1.27	1.29	1.59	13	10	17	10	10	13.3	
LSD 1		Δ-0.00	)5***	B-0.0	N52***	C=0.01		Δ-0.0	069***	B-0	071***	C=0.16		
LOD I	70	Availab						Availab						
	0%	12.3		15.0	13.0	14.0	13.5	61	67	69	65	66.	65.6	
>	1%	9.50	10.5	11.0	10.0	10.5	10.3	43	54	55	63	65	56.0	
Sandy soil	2%	8.50	9.50	10.0	9.00	9.00	9.20	43	46	48	44	47	45.6	
Sa	3%	7.00	8.50		7.50	8.00	7.90	36	40	45	34	42	39.4	
	Mean (B)	9.33	10.5	11.1	9.87	10.3	7.00	45.8	51.7	54.2	51.5	55	0011	
Soil (		0.00			0.0.		10.2	10.0	0	0	00	- 00	51.6	
	0%	10.5	11.0	11.5	10.5	11.0	10.9	41	53	55	52	53	52.8	
sno	1%	8.50	9.50	9.50	8.50	9.00	9.00	42	41	43	46	42	42.8	
are soil	2%	6.50		8.00	7.50	7.50	7.40	30	33	35	32	32	32.4	
Calcareous soil	3%	6.00	6.50	7.00	6.00	6.83	6.46	24	26	28	26	28	26.5	
O	Mean (A)	7.00	8.62	9.00	8.10	8.58		36.7	38.2	40.2	39.0	38		
Con.R	emedies						1						1	
means		8.60	9.56	10.0	9.00	9.47		41.2	45.0	47.2	45.2	46.9		
Soil (	C)						8.44						38.6	
LSD 1	%	A=0.0	98***	B=0.	.101***	C=0.28	***	A=0.	098**	* B=0	).10*** (	C=0.16'	**	

(A)=Type and Concentration. Remedies,B=concentration cured oil %,C = soil.

#### REFERENCES

- Abii, T. A. and Nwosu, P. C. (2009). The Effect of Oil- Spillage on the Soil of Eleme in Rivers State of the Niger Delta Area of Nigeria. Res J Environ Sci 3(3):316 320.
- Badawy, M. I. and Emababy, M. A. (2010). Distribution of polycyclic aromatic hydrocarbons in drinking water in Egypt. Desalination. 25: 34-40.
- Black, C. A. (1983). Methods of Soil Analysis, Part I and II, Soil Sci. Soc. Am. Inc. Puble., Madsison, Wisc., USA.
- Brian, K (1977). Soil Processes. 1st Edition. Allen George Unwin. London.
- Chaudhry, Q. M., Blom-Zandstra, S. Gupta and Jone, E. J. (2005). Utilising the synergy between plants and rhizosphere microorganisms to enhance breakdown of organic pollutants in the environment. Environmental Science Pollution Research, 12: 34–48.
- Chibuike, G. U. and Obiora, S. C. (2014). Heavy metal polluted soils: effect on plants and bioremediation methods. Hindawi publishing corporation, Applied and Environmental Soil Science V. 2014, Article ID 752708, 12 pages http://dx.doi.org/10.1155/2014/752708.
- Ekundayo, E. and Obuekwe, O. (2000). Effects of an oil spill on soil physicochemical properties of a spill site in a typic udipsamment of the Niger delta basin of Nigeria. Environmental Monitoring and Assessment, 60 (2): 235–249.
- Essien, O. E. and John, I. A. (2010). Impact of Crude-Oil Spillage Pollution and Chemical Remediation on Agricultural Soil Properties and Crop Growth. J. Appl. Sci. Environ. Manage. Vol. 14 (4) 147–154. Full-text Available Online at www.bioline.org.br/ja.
- Euliss K., Ho, C. H., Schwab., A. P., Rock, S. and Banks, M. K. (2008). Greenhouse and field assessment of phytoremediation for petroleum contaminants in a riparian zone. Bioresource Technology, 99: 1961–1971.
- Hisayoshi H. (2001). Effects of NPK Elements on Growth and Dry Matter Production of Common Buckwheat in Andosol. Institute of Agriculture and Forestry, Univ. of Tsukuba, Tsukuba, Japan. The proceeding of the 8th ISB:16-21(2001)
- Holliday, G.H. and Deuel, L.E. (1993). Annual Tech. Conference and Exhibition, Houston.
- Ian Grange (2001). The influence of soil surface management practices on the nutrient status and physical properties of calcareous soils in Thailand. International workshop on nutrient balances for sustainable agricultural production and natural resource management in Southeast Asia. Bangkok, Thailand, 20-22 February.
- Ismail, S. S. (2000). Contamination of the new desert lands near petroleum wells at Ras-Sudr. M.Sc. Thesis, Fac. of Agric., Cairo Univ., Egypt.
- Kelechi L. N., Modupe O. A. and Oboh, B. O. (2008). Growth and performance of Glycine max L. (Merrill) grown in crude oil contaminated soil augmented with cow dung. Nature and Science, 6 (1), ISSN: 1545-0740, naturesciencej@gmail.com.

- Kisic, I., Mesic, S. and Basic, F. (2009). The effect of drilling fluids and crude oil on some chemical characteristics of soil and crops. Geoderma, 149 (3–4): 209–216.
- Kshirsagal, S. and Aery, N. C. (2007). Phytostabilization of mine waste: Growth and physiological responses of (*Vignaunguiculate* L.) Walp. J. Environ. Biol., 28: 651-654.
- Leo, C. O. and Iruka, N. (2007). An appraisal of the impact of petroleum hydrocarbons on soil fertility: the Owaza experience. Afr. J. Agric. Res., 2:318-324.
- Liang, Y., Zhang, X., Wang, J. and Li, G. (2012). Spatial variations of hydrocarbon contamination and soil properties in oil exploring fields across China. J. Hazard. Mater. 241–242, 371–378.
- Lin, Q. and Mendelssohn, I. A. (2012). Impacts and recovery of the deepwater horizon oil spill on vegetative structure and function of coastal salt marsh in the northern Gulf of Mexico. Environmental Science & Technology, 46 (7): 3737–3743.
- Marchand, M., Bodennec G., Caprais, J. C. and Pignet, P. (1982). Report of the NOAA-CNEXO Joint Scientific Commission, 143-157.
- Michael, A. M. and Ojha, T. P. (2006). Principles of Agricultural Engineering Vol. II. 5th, Edition, Jain Brothers, New Delhi, pp. 331 390.
- Mille, G., Almallah, M., Bianchi, M., Van Wambeke, F. and Bertrand, J. (1991). Effect of salinity on petroleum biodegradation. Fresen. J. Anal. Chem. 339, 788–791.
- Mukhopadhyay, S., Hashim, M. A., Sahu, J. N. and Gupta, B. S. (2012). Performance of a biosurfactant obtained from Sapindus mukurossi in removing cadmium from soil, 14th Asia Pacific Confederation of Chemical Engineering Congress, 21-24 Feb. 2012.
- Osuji L. C., Egbuson E. J. G. and Ojinnaka, C. M. (2005). Chemical reclamation of crude-oil- inundated soils from Niger Delta, Nigeria. Chem. Ecol. 21(1): 1-10.
- Page, A. L., Miller R. H. and D. R. Keeny (1982). "Methods of Soil Analysis".
  Part 2. Chemical and Microbiological Properties, Second Edition, Madison, Wisconsin, USA.
- Pena, A., Palma, R. and Mingorance, M. D. (2011). Transport of dimethoate through a Mediterranean soil under flowing surfactant solutions and treated wastewater, Colloids and Surfaces A: Physicochem. Eng. Aspects, 384: 507–512.
- Pernar N., Baksic D., O Antonic, M Grubesic, I Tikvic and M Trupcevic (2006). Oil residuals in lowland forest soil after pollution with crude oil. Water Air and Soil Pollution, 177: 267–284.
- Rhoades, J. D. (1996). Salinity: Electrical conductivity and total dissolve solids. Pp. 417-436. In: Sparks, D.L. (Ed). Methods of Soil Analysis. Part 3 Chemical methods. SSSA. Madison, WI. USA.

- Rhodes, A.H., Hofman, J. and K.T. Semple (2008) Development of phenanthrene catabolism in natural and artificial soils. Environ. Pollut. 152, 424–430.
- Roch F. and Alexander, M. (1995). Biodegradation of hydrophobic compounds in the presence of surfactants. *Environmental Toxicology and Chemistry*, 14(7):1151–1158.
- Ryan, J., S. Garabet, K. Harmsen and Rashid, A. (1996). A soil and plant Analysis Manual Adapted for the West Asia and North Africa Region. ICARDA, Aleppo, Syria. 140pp.
- SAS institute (1985). SAS User's guide: statistics. 5. ed. Cary, N.C., 956p.
- Semple, K.T.; Morriss A.W.J. and Paton, G.I. (2003). Bioavailability of hydrophobic organic contaminants in soils: Fundamental concepts and techniques for analysis. Eur. J. Soil Sci. 54, 809–818.
- Soltanpour, P. N. and Schwab, A. P. (1977). A new soil test for simultaneous extraction of macro- and micro-nutrients in alkaline soils, Soil Sci. Plant Anal.; 8(3): 195-207.
- Sutton N. B., Maphosa F. and Morillo, J. A. (2013). Impact of long-term diesel contamination on soil microbial community structure. Applied and Environmental Microbiology, 79 (2): 619–630.
- Thomas, G.W. (1996). "Soil pH and Soil Acidity", pp. 475-490. In: Sparks, D.L. (ed.). Methods of Soil Analysis, Part 3: Chemical Methods, SSSA Book Series 5, Madison, WI., USA.
- UNEP/IOC/IAEA (1992). Determination of petroleum hydrocarbons in sediment. Reference standard methods for marine pollution studies no. 20, UNEP, Nairobi, Kenya, pp. 75.
- US-EPA (1997). Test methods for evaluating solid waste. SWS-846. update 111, USEPA office of water, Washington DC., USA.
- Wachs W. and Hayano, S. (1962). The critical micelle concentrations of fatty acid monoesters of the sucrose derivatives and their significance in the hydrophilic-lipophilic balance. Kolloid Z u Z Polymere 181:139–144.
- Wang G-D, C. X-Y, (2007) Detoxification of soil phenolic pollutants by plant secretory enzyme, phytoremedation, Humana Press, Totowa, 49–57.
- Wang X. Y, Feng J. and Zhao, J. M. (2010). Effects of crude oil residuals on soil chemical properties in oil sites, Momoge Wetland, China. Environmental Monitoring and Assessment, 161 (1): 271–280.
- Wang Y., Feng J., Lin q., Lyu X., Wang X. and Wang G. (2013). Effects of Crude Oil Contamination on Soil Physical and Chemical Properties in Momoge Wetland of China. Chin. Geogra. Sci. 2013 Vol. 23 No. 6 pp. 708–715.
- Wenjun, Z. and Lizhong, Z. (2008). Enhanced soil flushing of phenanthrene by anionic-nonionic mixed surfactant, Water Research, 42 (1-2): 101-108
- Whitten, K. W., Gailey, K. D. and Davis, R. E. (1985). General Chemistry 3rd Ed. Sounteys Holder Sunburst Series.

تقييم تأثير بعض المعالجات العضوية علي خواص التربة و المحصول. محمود عبد الجواد أحمد إسماعيل ، حسين محمود خليل وصيام حسن عبدالغنى معهد بحوث الأراضي والمياه والبيئة – مركز البحوث الزراعية – الجيزة – مصر.

أجريت هذه الدراسة لتقدير مدى كفاءة بعض المعالجات العضوية في تقليل تركيز بعض ملوثات التربة البترولية وكذلك دراسة تأثير كل من الملوثات والمعالجات على بعض خصائص التربة وعلى إنتاجية المحصول وامتصاصه لبعض العناصر الغذائية. أجريت تجربة أصبص تم فيها اختيار نوعين من التربة هما الرملية والجيرية، وكان قد تم تلويثهما بنسب 1 ، 2 ، 3 % من زيت البترول الخام وزراعتهم في موسم سابق حيث تم تجهيزها لمعالجتها. وتم إضافة معالجين وهما Triton x-100 و potassium oleate بمعدلات (غير معالج) ، 1 % ، 3 %. زرعت الأصص ببذور الشعير وأخذت عينات من نبات الشعير في نهاية التجربة. أدى استخدام المعالجين إلى زيادة تركيزات النيتروجين والفوسفور والبوتاسيوم في العينات المعالجه عنها في العينات الغير معالجة حيث كانت هناك اختلافات معنوية في هذه التركيزات في نبات الشعير والتربة بعد إضافة المعالجين المستخدمين ولكن الفروق كانت أكبر قليلاً بعد استخدام Triton x-100. كما أدى استخدام هذان المعالجان إلى زيادة محدودة في قيم ال EC و PH . كما أن استخدام هذه المعالجات ساهم بنسبة كبيرة في تقليل تركيز الملوثات الموجودة في التربة نتيجة تلويثها بزيت البترول الخام (الهيدروكربونات والعناصر الثقيلة) ، فمثلاً أدى استخدام Triton x-100 إلى تقليل تركيز النيكل بنسب وصلت في بعض العينات إلى 55 % كما قلل من تركيزات بعض الهيروكربونات إلى معدلات وصلت إلى 54 % مما يؤكد كفاءة هذه المعالجات المستخدمة. .هذه النتيجة تؤكد على أهمية هذه العلاج العضوي للحد من الأثار الضارة على خصائص التربة المعالجة.