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Remediation of Oil Polluted Soil

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ORGANIC (agrolic) and inorganic (bentonite) amendments were used to remediate oil polluted soils. Application of bentonite and agrolic at rate of 6 % by weight significantly decreased heavy metals concentrations in the oil polluted soils. The values decreased by about 25-27 % , 20 – 23% and 13-15 % in oil polluted soils supplemented with agrolic and about 30-32, 30-32 and 23-25 % in oil polluted soils supplemented with bentonite for oil pollution rate 1.5 ; 3 and 4.5 %, respectively.

Total petroleum hydrocarbon (TPH) decreased by about 40-44 % and 18-22 % in oil polluted soils supplemented with bentonite and agrolic, respectively.

Application of bentonite or agrolic remedies significantly enhanced the percent of germination, plant height, and dry matter of corn and wheat. Dry matter yield of bentonite treated soil was 6-11 % greater than agrolic treated ones. Application of bentonite and agrolic significantly decreased the concentrations of Fe, Mn, Zn, Pb, Cu and Cd by about 35-42 % and 25-32 % for oil polluted soils supplemented by bentonite and agrolic, respectively.

Keywords: Crude oil, Pollution, Remedy, Agrolic, Bentonite.

Remediation of contaminated soils and groundwater has gained more attention as a result of the discovery of thousands of contaminated sites, such as places with under ground storage leakage or industrial wastes disposal. The most common method for remediating contaminated site was excavation followed land filling or incineration; however, excavation/land filling can not destroy contaminants and incineration could cause a secondary pollution such as formation of polychlorinated binezofurans (PCDFs) or polychlorinated dibenzo– P– dioxins ($PCDD_s$). Due to the limitation of these conventional methods, various on site and in site treatment technologies were developed to remediate contaminated sites.

Organic supplements (poultry manure, sawdust, yeast and peptone water) modified soil physical, chemical and biological properties in oil polluted soil and enhanced plant growth (Amadi *et al.*, 1993). Shuman (1998) pointed out that organic amendments decreased the available Cd and Pb. Frang and Wang (1999) showed that lime amendment (0.6-1.6%) significantly reduced water soluble and DTPA extractable Cu, Mn, Zn, and Ni. A lime amendment of $\leq$ 1% is recommend. Curtis and Lammey (1998) pointed out how intrinsic remediation can reduce the effect of free floating hydrocarbons.

The present work was undertaken to appraise the effect of supplementing bentonite and agrolic as remedies to oil polluted soil on plant growth and assess the heavy metals and hydrocarbon contents in this regard.

Material and Methods

A surface sandy soil (0-15 cm) from Ras-Sudr, South Sinai, Egypt near by a petroleum well was used in this study. Soil pH ranged from 7.2-7.6, electrical conductivity ($EC_{1:2.5}$) 0.3-1.9 dS/m, organic matter 0.1-0.3%, $CaCO_3$ 34-48 %, cation exchange capacity (CEC) 2-6.4 cmol/kg , sand 60-86 %; Silt 8-14 %, and clay 4-14%. Soil properties were determined according to the method described by Jackson (1967); Piper (1950) and Tucker (1971). Total content of heavy metals were extracted by digestion in mixture of nitric, sulfuric and perchloric acids (Hesse, 1971).

Crude oil was obtained from the oil well at about ten kilometer from Ras-Sudr. Agricultural Experimental Station of the Desert Research Center, South Sinai. The heavy metals of the oil were extracted according to the method described by Price (1972), and were measured by atomic absorption spectrophotometer (Perken-Elmer model 2083). Total petroleum hydrocarbons (TPH) were extracted according to the method described by Farag *et al.* (1990) and were determined using GLS apparatus (GLS pyenicam pa 4550 capillary chromatography). Some chemical properties of the used crude oil are presented in Table 1.

TABLE 1. Some chemical properties of the used crude oil .

a- Heavy metals μg g^{-1}

Fe	Mn	Zn	Pb	Cu	Cd
8960	462	95	37	14.3	6.0

b- Hydrocarbons (%)

Compounds		%	Compounds		%
Dodecane	C_{12}	0.85	Teracosane	C_{24}	2.54
Trtradecane	C_{14}	1.33	Hexacosane	C_{26}	2.31
Hexadecane	C_{16}	2.10	Octacpane	C_{28}	10.08
Octadecane	C_{18}	3.55	Triacontane	C_{30}	46.04
Eicosane	C_{20}	3.60	Squalane	C_{31}	2.23
Docosane	C_{22}	3.39	Dotriacontane	C_{32}	4.80
Total petroleum hydrocarbons					82.82

Two different remedies were used, namely agrolic and bentonite. Agrolic is a concentrated humic acid (84 %) at granular shape. It was used as an organic remedy. Agrolic was obtained from Wadi El-Neel Company of Agricultural Development. The composition of the agrolic used is presented in Table 2. Bentonite was obtained from Quse El-Sagha Mining, Ministry of Industry. It was used as an inorganic remedy. The chemical and physical properties of bentonite are presented in Table 3.

TABLE 2. Some chemical properties of the used Agrolic.

EC (dS/m)	pH	O.M %	CEC (cmol/kg)	S %	N %	Heavy metals (μg g^{-1})					
						Cd	Pb	Cu	Zn	Mn	Fe
3.2	4.0	84	82.5	2.0	1.0	0.6	3.5	3.0	16.5	200	2000

TABLE 3. Some physical and chemical properties of the used bentonite.

Particle size distribution (%)				EC (dS/m)	pH	CEC (cmol/kg)	Heavy metals (μg g^{-1})					
Coarse sand	Fine Sand	Silt	Clay				Cd	Pb	Cu	Zn	Mn	Fe
10	10	20	60	2.6	7.9	64.5	0.3	2.6	1.8	15.0	200	2600

Green house experiment

A pot experiment was conducted during the season (April, 1996-February, 1997) in the green house at the Desert Research Center, using maize (*Zea mays*) followed by wheat (*Triticum vulgare* L.). Soil was contaminated with crude oil by spraying and continuous mixing the soil with the crude oil to reach the contamination level (0, 1.5, 3 and 4.5%). The soil was then placed into pots measuring 20 cm inside diameter and 25 cm height. The above mentioned rates of crude oil were combined with two different remedies (agrolic and bentonite), at rate of 6 % of the pot weight. Three replications were used for each treatment in a complete randomized design. The sketch diagram of treatments used in pot experiment is shown in Fig. 1.

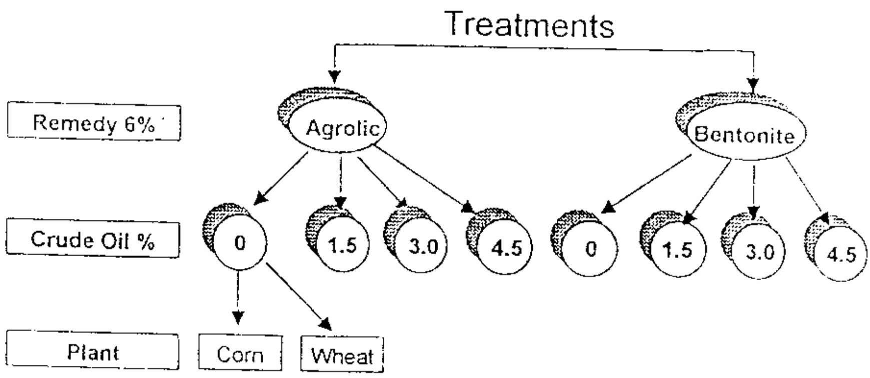

Fig. 1. Sketch diagram of treatments used in the pot experiment.

Sixteen maize (*Zea mays*) seeds were sown per each pot on the 20th of April 1996. After 10 days from sowing, plants were thinned to 8 plants per pot. Recommended doses of chemical fertilizers (150 kg/fed superphosphate, 100 kg/fed ammonium nitrate and 50 kg/fed potassium sulphate), were added for each pot. On the 25th of June 1996 (40 days from sowing) plants were harvested.

The same previously used pots were cultivated on the 20th of November 1996 with 20 seeds of wheat (*Triticum vulgare* L.) per pot. Ten days after sowing plants were thinned to 12 seedlings per pot. All pots were fertilized with the recommended doses NPK. Irrigation was performed to keep soil moisture content at field capacity. On the 5th of February 1997 (65 days after sowing) plants were harvested. Dry matter at 70 C° of corn and wheat plants were determined and were digested using mixture of sulfuric nitric and perchloric acids (Van Schwnburg, (1968). Soil samples were taken from each pots (after corn and wheat harvesting) air dried and subjected to chemical analysis.

Heavy metals were determined using atomic absorption spectrophotometer (Perken Elmer Model 2083).

Results and Discussion

Heavy metals concentrations in soils

Application of bentonite or agrolic significantly decrease the Cd, Pb, Cu, Zn, Mn and Fe concentrations in the oil polluted soils (Fig. 2). The values of Cd, Pb, Cu, Zn, Mn and Fe in highly oil polluted soils (4.5 %) were 3.8, 26.5, 19.2, 89.4, 460 and 6850 $\mu g\ g^{-1}$, respectively for corn and 3.1, 18.1, 12.3, 58.1, 325 and 6375 $\mu g\ g^{-1}$, respectively for wheat. These values decreased by about 25-27, 20-23 and 13-15 % in oil polluted soils supplemented with agrolic, and about 30-32, 30-32, and 23-25 % in oil polluted soils supplemented with bentonite for oil pollution rate (1.5, 3.0 and 4.5 %), respectively. Bentonite was more effective in reducing heavy metal with about 5-10 % lower than agrolic.

Hydrocarbon concentrations in soils

Total petroleum hydrocarbon concentrations (TPH) were 149.7, 194.6 and 245.8 $\mu g\ g^{-1}$ in soils polluted with oil at rates of 1.5, 3.0 and 4.5 %, respectively. Application of bentonite and agrolic significantly decreased theses values. Oil polluted soils supplemented with bentonite showed the greatest decrease in total petroleum hydrocarbons. The decrease in TPH was about 40-44% in oil polluted soil supplemented with bentonite, and 18-22 % for oil polluted soils supplemented with agrolic (Table 4).

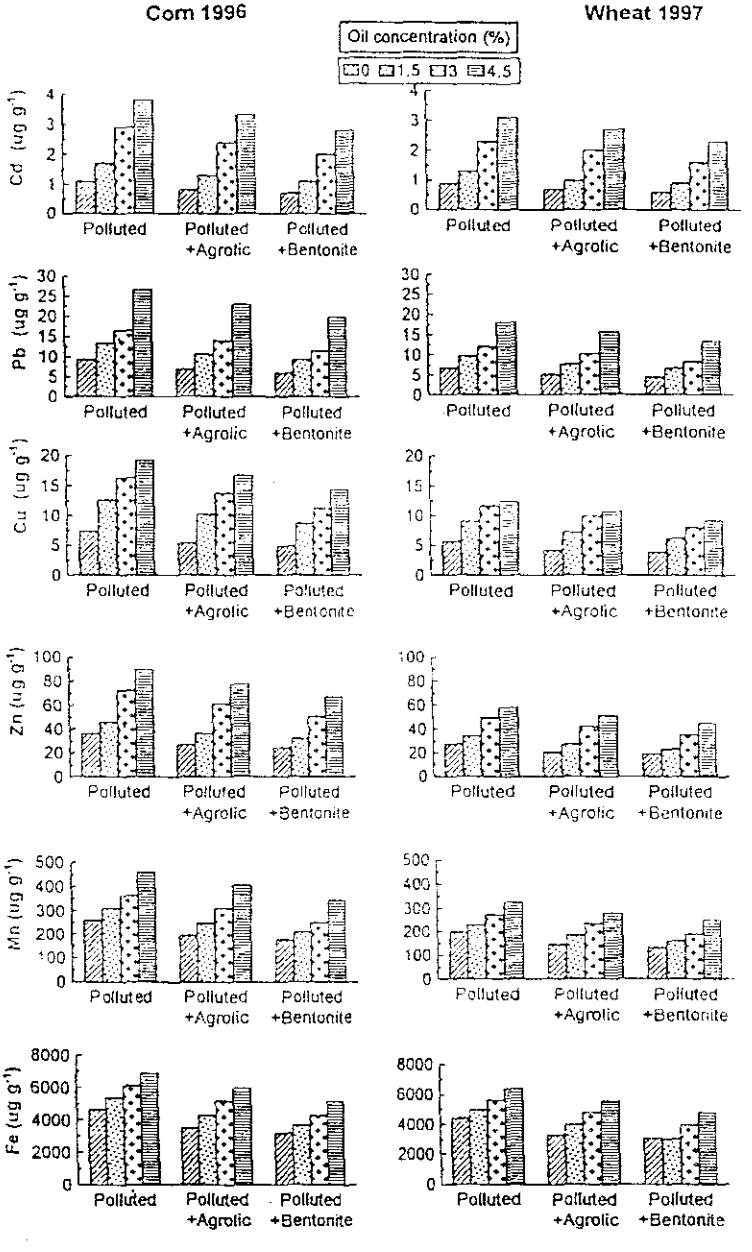

Fig. 2. Total concentration of heavy metals (μg g^{-1}) in oil polluted soil supplemented with agrolic and bentonite remedies.

TABLE 4. Total concentration (µg g^{-1}) of hydrocarbons in polluted soils supplemented with agrolic and bentonite remedies.

Compound	0 Control	Oil Concentration (%)								
		1.5			3.0			4.5		
		Untreated	Agrolic	Bentonite	Untreated	Agrolic	Bentonite	Untreated	Agrolic	Bentonite
Dodecane C_{12}	0.02	1.3	1.2	0.5	2.7	1.6	1.2	4.5	3.4	3.2
Tetradecane C_{14}	0.09	1.8	1.3	0.9	2.3	2.1	1.7	6.2	3.6	2.2
Hexadecane C_{16}	0.04	8.9	6.2	2.8	12.7	9.8	4.9	17.0	14.1	8.1
Octadecane C_{18}	0.21	8.3	4.5	4.2	14.0	16.2	8.3	16.6	19.5	11.7
Eicosane C_{20}	0.10	2.7	1.6	1.2	8.2	2.8	2.7	15.4	5.2	3.8
Docosane C_{22}	0.48	19.1	17.1	10.1	20.6	14.5	12.6	27.1	17.1	15.9
Teracosane C_{24}	0.06	5.9	3.4	2.0	8.7	5.6	3.9	15.0	8.2	7.1
Hexacosane C_{26}	0.10	6.8	5.4	3.3	14.1	10.5	6.8	16.8	12.2	9.4
Octacpane C_{28}	0.84	34.1	28.6	21.2	35.2	25.3	23.9	38.0	30.0	25.3
Triacontane C_{30}	1.21	35.3	33.0	23.5	37.4	34.8	27.4	39.2	37.6	29.3
Squalane C_{31}	0.30	13.9	11.8	8.4	26.2	25.3	13.6	32.6	25.7	16.4
Dotriacontane C_{32}	0.23	11.6	9.2	5.3	12.5	11.4	9.8	17.4	16.8	14.3
Total	3.68	149.7	123.3	83.4	194.6	159.9	116.8	245.8	193.4	146.7

Growth parameters

Crude oil decreased the germination of both wheat and corn. The application of agrolic or bentonite remedies to oil polluted soils enhanced the percent of germination of both plants (Table 5). The increase in germination is attributed to the ability of agrolic and bentonite to absorb oil applied to soil thus reduce the degree of contact with corn and wheat seeds. They also reduce the waxy effect of oil. The increase in germination percentage is more pronounced when polluted soils supplemented with bentonite, as the greatest germination values of 89 and 81 % were recorded for corn and wheat, respectively.

Application of bentonite and agrolic remedies have a pronounced effect on plant growth. Plant height as a performance to plant growth showed the least in oil polluted soils (Table 5). The greatest values were observed in the oil polluted soils supplemented with bentonite or agrolic remedies. The plant height increased by an average of 12-32 % and 15-50 % with agrolic and bentonite, respectively.

Application of bentonite and agrolic remedies significantly increased the dry matter yields compared to polluted soils (Table 5). The highest dry matter values were recorded in the lowest oil polluted soil (1.5 %) supplemented with bentonite or agrolic. The percent of dry matter increase is about 30, 15 and 13% in the first season and 45,24 and 20 % in the second season more than that of the oil polluted with 1.5, 3, and 4.5 %, respectively.

Oil polluted soils supplemented with bentonite showed greater dry matter yield of both corn and wheat compared to those supplemented with agrolic. The percent of dry matter yield of bentonite supplemented soils is 6-11 % high relative to that of agrolic supplemented ones. Application of remedies is beneficial in improving soil physical, chemical and biological properties, and accordingly reduces the hazardous effect on plant growth.

Heavy metals concentration in plants

The data presented in Fig. 3 indicate that uptake of Cd, Pb, Cu, Zn, Mn and Fe were enhanced in polluted soils. The higly polluted soil was, high as the concentration of these elements in both wheat and corn plants was high. Application of bentonite or agrolic significantly decreased the concentration of heavy metals in both plants. Bentonite showed the greatest effect in decreasing the concentrations of Cd, Pb, Cu, Zn, Mn and Fe in plant than agrolic did. The decrease was about 35 – 42 % for oil polluted soils treated with bentonite, while it was 25-32 % for oil polluted soils treated with agrolic.

TABLE 5. Growth response of corn and wheat seedlings grown in oil polluted soils supplemented with agrolic and bentonite remedies.

Plants	Treatments		Oil concentration (%)			
			0	1.5	3.0	4.5
Corn 1996	Polluted and without amendments	Germination %	95.0	80.0	63.0	50.0
		Shoot length (cm)**	57.3	48.0	34.5	26.0
		Dry matter (g/pot)*	20.3	17.2	12.7	9.6
	Polluted + Agrolic	Germination %	96.0	86.0	67.0	56.0
		Shoot length (cm)**	60.0	54.2	41.8	34.5
		Dry matter (g/pot)*	26.2	22.3	14.6	10.8
	Polluted + Bentonite	Germination %	97.0	89.0	70.0	59.0
		Shoot length (cm)**	60.5	55.1	44.8	39.0
		Dry matter (g/pot)*	28.4	24.9	15.8	11.5
Wheat 96/97	Polluted and without amendments	Germination %	94.0	70.0	60.0	40.0
		Shoot length (cm)***	25.8	21.0	14.9	10.0
		Dry matter (g/pot)*	18.5	12.8	10.7	8.5
	Polluted + Agrolic	Germination %	95.0	78.0	65.0	45.0
		Shoot length (cm)***	26.0	23.5	18.2	13.8
		Dry matter (g/pot)*	24.0	16.8	12.3	9.5
	Polluted + Bentonite	Germination %	96.0	81.0	68.0	48.0
		Shoot length(cm)***	27.0	24.0	20.2	15.5
		Dry matter (g/pot)*	26.8	18.7	13.3	10.2

* Means of 3 replicates.
** Means of 24 replicates.
*** Means of 36 replicates.

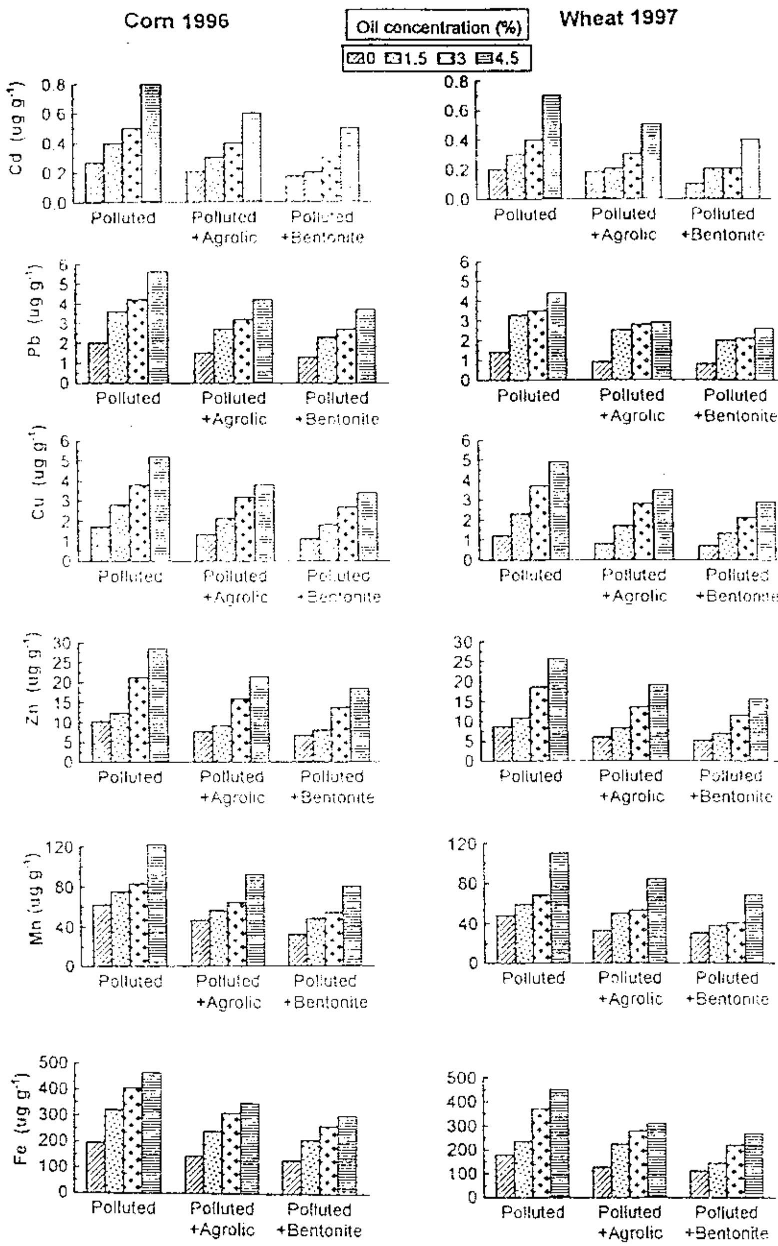

Fig. 3. Concentration of heavy metals (µg g^{-1}) in corn and wheat plants grown in oil polluted soil supplemented with agrolic and bentonite remedies.

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معالجـــة الأراضى الملوثة بالبترول

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فى تجربة أصص استخدم الأجروليك كمادة عضوية والبنتونيت كمادة غير عضوية لإصلاح الأراضى الملوثة بالبترول. ولقد بينت الدراسة أن استخدام هذه المواد بمعدل ٦٪ بالوزن أدى إلى نقص تركيزات العناصر الصغرى فى الأراضى الملوثة. وأن هذا النقص وصل إلى ٢٥ - ٢٧٪ ، ٢٠ – ٢٣ ٪ ، ١٣ – ١٥٪ عند إضافة الأجروليك وكان النقص ٣٠ – ٣٢ ، ٣٠ – ٣٢ ، ٢٣ – ٢٥ ٪ عند إضافة البنتونيت للأراضى الملوثة بالبترول بنسب ١,٥ ، ٣ ، ٤,٥ ٪ على الترتيب.

كما أوضحت الدراسة نقص هيدروكربونات البترول فى التربة بنسبة ٤٠ – ٤٤٪ عند إضافة البنتونيت وبنسبة ١٨ – ٢٢ ٪ عند إضافة الأجروليك.

ولقد أدت إضافة البنتونيت أو الأجروليك إلى الأراضى الملوثة إلـــى زيادة نسبة الإنبات وطول النباتات والمادة الجافة للذرة والقمح. وكانت الزيادة أكثر بنسبة ٦ –١١٪ فى حالـــة إضافـــة البنتونيت عن الأجروليك. ولقد أدت إضافة المعالجات إلى نقص تركيز عناصر Fe, Mn, Zn, Cu, Pb, Cd فى التربة بنسبة ٣٥ – ٤٢٪ عند إضافة البنتونيت و٢٥ – ٣٢٪ عند إضافة الأجروليك للأراضى الملوثة.