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EFFECT OF POLLUTION WITH PETROLEUM ON SOME SOIL CHARACTERISTICS AND PLANT GROWTH

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ABSTRACT

Petroleum products are complex mixtures of hundreds of hydrocarbon compounds. Petroleum has been recognized as a potential environmental contaminant. This research was undertaken to evaluate the effect of petroleum hydrocarbon on soil characteristics and seeds germination in arid lands. Results indicated that bulk density and real density of the polluted samples are relatively higher and lower respectively then the corresponding values of the unpolluted soils. Percent ages of the clay fraction obtained with and without removing the cementing agents showed high and low values for % clay fraction respectively. Low calcium carbonate content was found in the polluted samples as a result of solubilization effects of the petroleum products on calcium carbonate particles. ECe values were very high in the polluted samples (ECe = 28.6 - 82.5 dS/m) and very low in the unpolluted samples (ECe = 2.75 - 2.79 dS/m). Soluble calcium and sulphat ions were the dominant ions in the saturation extract of unpolluted soil samples. Organic matter contents were high (4.94%) in the polluted soil and Low in the unpolluted soil (0.54%). Soil polluted with hydrocarbon was very high (7.13-7.5%) in the unpolluted soil and very low (0.63-0.71%) in the polluted soil. Total elemental contents shows that the most important metals with regard to potential hazards in the contaminated soils, are Cr, Pb, and Ni. Other heavy metals indicated low to medium concentration either in petroleum polluted or the non polluted soils. The concentration of toxic elements in the tested soils could be derived from petroleum pollution and/or from it's chemical weathering particularly under the relatively low pH of the polluted soils. Results indicated no barley seed emergence after 14 days in the polluted soil even after several leaching to alleviate the high level of salt concentrations in the polluted soil. The data reflect the serious effects of petroleum products on the deterioration of soil characteristics which reflected on the emergence of barley seeds.

INTRODUCTION

Soil pollution is of an environmental concern and may lead to the more serious problem of groundwater contamination. Petroleum has been recognized as a potential environmental contaminant since the beginning of the Twentieth Century. Scientific literature on the subject was sparse until after World War II when reports of the effects of oil pollution began to appear with greater frequency. The accumulated literature on this well-studied contaminant is vast, covering topics as diverse as analytical chemistry, chemical fate, oil spill prevention and response, mitigation and restoration, economic and social analysis, and biological effects on all forms of plant and animal life in saltwater, freshwater, and terrestrial environments. Total petroleum hydrocarbons (TPH) is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil. Crude oil is used to make petroleum products, which can contaminate the environment. Because there are so many different chemicals in crude oil and in other petroleum products, it is not practical to measure each one separately. However, it is useful to measure the total amount of TPH in situ. Petroleum products are complex mixtures of hundreds of hydrocarbon compounds, ranging from light, volatile, short-chained organic compounds to heavy, long-chained, branched compounds. The exact composition of petroleum products varies depending upon (1) the source of the crude oil

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(crude oil is derived from underground reservoirs which vary greatly in their chemical composition) and (2) the refining practices used to produce the product. Many of the most environmentally significant components of petroleum hydrocarbons such as (benzene, toluene, ethyl benzene, and the xylenes,(MTBE and some PAHs polynuclear aromatic hydrocarbons) and can be biodegraded under the proper environmental conditions. However, (BTEX some other PAHs, (methyl tertiary butyl ether and MTBE a gasoline additive) and other components of petroleum hydrocarbons may not readily biodegrade as reported by **U.S. EPA Remedial Technology (1999).** Generally, petroleum hydrocarbons that are most mobile in the environment (except for MTBE) are also readily biodegraded. Once the more mobile and easily degradable petroleum hydrocarbons are removed, the remaining hydrocarbons, which are not readily degraded, can still pose a high risk in the immediate vicinity of the area. **Sundaram and Islam, (1994)** presented a scale physical model studies for petroleum contaminant removal using surfactant solutions. Scaling criteria are selected in such a way that a realistic representation of the decontamination process is possible. The proposed scaling approach meets all important requirements of this decontamination process which uses surfactant solutions. Results indicated that' the clean-up method has to be planned, according to the soils as well as the contaminant. In situ soil washing using surfactants shows great potential to remove hydrophobic organics from subsurface environments **Roy *et al* (1994)**. Soil organic matter (SOM) content has been implicated as the primary factor governing the interactions between organic contaminants and soil particles **(Gschwend and Wu, 1985; Rutherford *et al* 1992; Weber *et al* 1992).** Slow rates of desorption or mass transfer of contaminants from SOM matrices can render the soil washing process uneconomical for coarser material that may have large amounts of organic carbon. Mineral attributes of the soil or aquifer material, such as the presence of surface metal oxides, may also exert significant control on the extent to which SOM or organic contaminants adhere to the mineral domain of the soil particle **(Gu *et al* 1994; Kaiser *et al* 1998).** The main objective of this research was to evaluate the effect of petroleum hydrocarbon products on soil characteristics and plant germination in arid lands. Also, to evaluate the changes in soil characteristic in relation to the level of petroleum pollution in the soil profile.

MATERIALS AND METHODS

Soil Samples and Methods of Analysis: Five soil samples were collected in February 2008 from different locations around petroleum well (No. 139). The location of the well was about 90 km South of Deir Ezzor city and about 1.5 km west of the road between Deirezzor – AbuKamal west of Elsalihia village, Syria. Samples were collected as follows: two unpolluted soil samples were taken from surface and subsurface layers of soil profile representing wheat cultivated soil. Further two polluted soil samples (surface 0-20 and subsurface 20-40 cm) were collected from the soil nearly the petroleum well. The source of pollutions of these samples was the petroleum spills from the surrounding well. Soil sample No. 5 was taken from the heaps of the soil materials polluted with petroleum products from the well which were mixed with soil materials eroded from the surrounding soils.

All the collected soil samples were taken to the laboratory, air dried ground and sieved through a 2mm sieve. The soil samples were analyzed in the laboratory according to the standard methods. Percentages of the clay, silt and sand were carried out using the hydrometric method described by **Black (1965)** after carrying the appropriate pretreatments to remove soluble salts, $CaCO_3$ and organic matter from the samples. Percentages of the same fractions were carried out once again using the hydrometric method but without carrying the aforementioned pretreatments. Real density and bulk density were determined in disturbed and undisturbed soil samples respectively as described by **Black (1965).** Saturation water percentage (%SP) was determined gravimetrically. Soluble salts were measured electrometrically using an EC meter in the saturation paste extract. Soil pH and soluble cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anions (Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}) were determined in the same extract as described by **Richards (1954)**. Calcium carbonate content was determined according to **Allison and Moodie (1965).** Gypsum contents were determined by the standard method described by **Richards (1954)** which involves precipitation with acetone. Organic matter content was determined using dichromate oxidation method **Page *et al* (1982) .** Total elemental analysis using a representative sub-samples was carried after sample digestion using hydrofluoric acid in a closed vessel as described by **Jackson (1974).** Total Zn, Co, Ni, Cu and Pb were measured in the acid extracts using atomic absorption spectrometer (AAS) according to **Page *et al* (1982)** while other elements in the extracts were measured by Inductively Coupled Plasma Emission Spectrometer (ICP)**.** Polluted petroleum byproducts were determined in the polluted and unpolluted samples according to **Palittapongarnipim *et al* (1998).**

Germination experiment: A pot experiment was carried out in the laboratory in order to determine percentage of emergency of barley seeded in the polluted and the unpolluted samples. One hundred gram portions of air dried soil samples were placed in a plastic container (capacity 250 cm^3) each over filter papers fixed at the bottoms of these containers. Barley seeds (10 seeds/ pot, *Hordeum vulgare L*., Giza/123 cultivar) were sown in the soil in August 17, 2008. The pots were irrigated with the tap water to aprox. Field capacity, and moisture content were kept constant by irrigation with tap water every other day. There were differences between the soils in absorbing the applied irrigation water. The polluted samples showed very low water infiltration particularly, the sample No. 3 while the unpolluted samples absorbed the applied water regularly and faster. The number of seedlings in each pot was recorded with time from the beginning of the experiment till August 31. Seeds in the polluted soil pots did not germinate within the aforementioned 14 days. The non germinated seeds were removed from the polluted soil pots (No.: 3, 4, and 5) then the polluted samples were leached several times using distilled water until the conductivity (EC_w) of the leachate was decreased to less than 4 dS/m. The leachate was collected and analyzed in the laboratory for EC, pH, and total alkalinity. The leached soil samples were ground and replanted by barley seeds 10 seeds/pot*, Hordeum vulgare L*., Giza /123 cultivar, then the pots were irrigated as reported before and the seedlings were counted.

RESULTS AND DISCUSSION

Data in **Table (1)** indicated that the studied soil samples have quite variable clay contents ranged from 6.39 - 16.7 % being relatively higher in the unpolluted surface soil sample (No.1) and the sample representigthe soil samples polluted with petroleum products, i.e. sample No.5. All the samples are loam to loamy sand texture. The polluted surface (0-20 cm) and subsurface (20-40 cm) soil samples seem to have less clay content than the unpolluted surface or subsurface ones. It appears also that bulk density and real density of the polluted samples were relatively higher and lower respectively than the corresponding ones of the unpolluted samples. The lower real density of the polluted soil samples can be attributed to the presence of petroleum materials which are of low density mixed with the soil. On the other hand, the relative increase in bulk density of the polluted samples may be attributed to the replacement of the petroleum materials instead of the gaseous phase in the voids of the soil. Data of % of each of the clay, silt, and sand fractions obtained without carrying out the pretreatments showed lower values for the clay fraction in the unpolluted and transported samples and on the other hand, relatively higher values in the sand fraction unlike the corresponding value of the polluted samples which showed no change in the clay fraction. These variations can be explained on the basis of flocculation process occurred for the clay particles by organic matter and or divalent cations existed in the sample since these flocculating agents are already present in the soil samples.

Data in **Table (2)** indicated that the studied soil samples have $CaCO_3$ contents ranging from 15.1 to 23.0 % being higher in the unpolluted surface and subsurface soil (29.5 and 30.2 %, respectively) and relatively lower in the polluted surface and subsurface soil. The lowest calcium carbonate content was found in the polluted sample taken from the heaped polluted soil materials. Lowering calcium carbonate content in the polluted samples could be related to the solubilizing effect of the petroleum products on calcium carbonate particles. Data indicated that ECe (dS/m) values were very high in the polluted surface and subsurface samples (ECe = 28.6 and 82.5 dS/m) well as the sample No 5 which was collected from the surface of the heaped-polluted soil (ECe 62.6 dS/m). Very lower EC values characterized in the unpolluted surface and subsurface soil (ECe = 2.75 and 2.79 dS/m, respectively). The increase in salinity as a result of soil pollution with petroleum products might be due to presence of soluble salts in the petroleum products or soluble effect of these products on some insoluble soil components. Data of soluble cations and anions indicated that calcium and sulphate ($SO_4^{2-)}$ ions were the dominant ions in the saturation extract of unpolluted soil samples (No. 1 and 2) while Na^+ and Cl^- ions were the dominant ions in all the polluted samples (No. 3, 4, and 5). It appears also that Na^+ and Ca^{2+} cations increased dramatically followed by Mg^{2+} cation in the soil paste extracts of the polluted samples compared with unpolluted soil samples, while Cl^- and SO_4^{2-} showed very high values in the polluted soil samples. Data indicated quite low pH values of the polluted samples ranging from 5.67 to 6.00, while the unpolluted samples have pH of 7.17 and 7.25 in the surface and subsurface layers respectively. It seems that pollution of soils by petroleum products decreased soil pH and hence increased the solubility of calcium carbonate and consequently a decrease in its content in soil. Therefore, increasing solubility of calcium carbonate as a result of decreasing soil pH and the introduction of NaCl with the polluted petroleum products seemed to be the main reasons for increasing salinity in the polluted samples. On the other hand, data indicated an inverse trend for the contents of gypsum in the polluted and unpolluted samples. Where it seemed to be relatively lower in the unpolluted subsurface soil and relatively higher in the polluted subsurface layer, which may be due to of gypsum formation from the excess of the calcium ions produced from the dissolved calcium carbonate as mentioned before. Organic matter contents in the polluted soil samples were quite high where they reached 4.94% in the surface layer sample of the soil. Lower organic matter content was recorded for the unpolluted soil (about 0.54%). On the contrary higher contents of organic matter in the polluted samples could be attributed to the organic constituents of the petroleum materials added to the polluted soil. Data for the total hydrocarbons and unhydrocarbon components of the polluted petroleum materials of the soil **(Table, 3)** indicated that hydrocarbons are very low (0.63-0.71%) in the unpolluted soil (sample Nos.1 and 2), while they were very high (7.13-7.5 %) in the polluted soil (sample Nos. 3 and 4). Sample No 5 indicated relatively lower percentage of the hydrocarbons. The most environmentally significant components of petroleum hydrocarbons were BTEX (benzene, toluene, ethyl benzene, and xylenes) and some PAHs (polynuclear aromatic hydrocarbons), **U.S. EPA Remedial Technology (1999).** The obtained data reflect the level of soil pollution by petroleum hydrocarbons which in turn, affected all the studied soil properties. Data also indicated that the non-hydrocarbon components were higher in all the studied polluted and unpolluted soil samples, ranging from (6.75-11.88%). The ratio of the hydrocarbons to the non-hydrocarbon components, which reflects more accurately the level of pollution, was relatively wide in the unpolluted soil (sample 1 and 2) and very close in the polluted soil (samples 3-5). Many of petroleum hydrocarbons such as BTEX and some PAHs can be biodegraded under the proper environmental conditions as reported by **U.S. EPA Remedial Technology (1999).** However, some PAHs, MTBE (methyl tertiary butyl ether, a gasoline additive) and other components of petroleum hydrocarbons may not readily biodegraded. Once the more mobile and easily degradable petroleum hydrocarbons are removed, the remaining hydrocarbons, which are not readily degraded, can still pose a high risk in the immediate vicinity of the area in which they remain.

Table (4) indicated the results of total elemental contents of the studied soils. It shows that the most important metals with regards to potential hazards in contaminated soils are Cr, Pb, and Ni. The other studied heavy metals indicated lower concentrations either in petroleum polluted or the non polluted soil samples. The concentrations of these toxic elements in the tested soils may be derived from petroleum pollution and weathering of natural background rocks particularly under the relatively low pH of the polluted soils. The contents of Cd in the non polluted soil were relatively higher probably due to the anthropogenic contamination of the soil. The relatively high contents of Ca, Mg, Na elements in the polluted soils might be derived mainly from the polluted petroleum products **Kabata-Pendias and Pendias, (1992).**

Germination experiment: Data in **Table (5)** show the results of germination trial of 10 barley seeds in the studied soil samples. No seedlings emergence could occur in the polluted samples (No. 3, 4 and 5) after 14 days while the unpolluted soils No. 1 and 2 showed germination of most of the seeds after almost 14 days. These data may reflect the serious effects of petroleum products on the deterioration of soil characteristics which negatively affected the emergence of barley seedlings. It is quite clear that the very high salt concentrations in the polluted soils beside the effects of petroleum products contributed together to preventing emergences of barley seedlings in these soils. Data in **Table (6)** show the results of barley seedling emergence in the polluted soils washed several times by distilled water to reduce their salinity level. It is indicated that germination of barley seeds has occurred after 4 and 8 days of the 1st irrigation in sample Nos.3 and 5 respectively, while no germination occurred in sample Nos.4. Data of water leached from the polluted samples **(Table, 7)** show that the salinity level of the final washing step was reduced to acceptable level for barley seed germination and for seedling to emergence while pH and total alkalinity levels although increased slightly, yet they seemed to be of no effect on the germination of the seeds. Therefore pollution with

Table 1. Physical properties of the tested soils

Soil Sample Nos.	Density g/cm^3		Particle size distribution (%)			Soil Texture	Hygroscopic water %	Granular analysis (%)		
	Bulk	**Real**	**Sand**	**Silt**	**Clay**			**Sand**	**Silt**	**Clay**
1- Non-polluted soil (0 -20 cm)	1.56	2.38	79.99	3.31	16.70	Loamy Sand	0.74	80.73	12.88	6.39
2- Non-polluted soil (20 -40 cm)	1.40	2.57	36.91	51.55	11.54	Loam	0.68	83.30	10.31	6.39
3- Polluted soil (0-20 cm)	1.60	2.11	72.99	20.62	6.39	Loamy Sand	2.01	88.15	15.46	6.36
4- Polluted soil (20 -40 cm)	1.45	2.26	67.4	26.21	6.39	Loamy Sand	1.61	72.99	20.62	6.39
5- Heaped surface polluted soil materials	1.71	2.44	34.33	48.97	16.70	Loam	1.69	42.06	51.55	6.39

Table 2. Chemical properties of the tested soils

Soil Sample Nos.	pH Soil paste	EC dS/m	CaCO$_3$ %	CaSO4. 2H2O %	O.M. %	Soluble anions m mol$_c$ L^{-1}				Soluble cations m mol$_c$ L^{-1}			
						CO3^{2-}	**HCO3$^-$**	**Cl$^-$**	**SO4^{2-}**	**Ca^2+**	**Mg^{2+}**	**K$^+$**	**Na$^+$**
1	7.17	2.75	30.2	1.23	0.54	-	2	10	15.65	14	6	0.25	7.4
2	7.25	2.79	29.5	0.98	0.52	-	2	10	15.75	16	5	0.25	6.5
3	5.78	28.6	23.0	1.15	4.94	-	10	245	32.75	160	18	0.75	109
4	6.00	82.5	19.4	1.72	3.78	-	20	730	80.75	220	50	0.75	560
5	5.67	15.1	15.1	1.89	1.03	-	2	840	22.5	250	32	0.5	582

Table 3. % Polluted petroleum materials (hydrocarbon and non hydrocarbon) in the studied soil samples

Soil sample Nos.	Polluted Hydrocarbons %	Organic non Hydrocarbons materials %	Total Hydrocarbons and non hydrocarbons materials %	Ratio
1	0.71	11.88	12.59	1:16.73
2	0.63	6.75	7.38	1:10.71
3	7.5	12.57	20.07	1:1.68
4	7.13	10.97	18.10	1:1.54
5	1.69	9.46	11.15	1:5.59

Table 4. Total elemental analysis of the studied soil samples (mg/kg soil)

Soil sample No. / Element (mg/kg)	1	2	3	4	5
Aluminium	1560	14334	14994	14884	30059
Boron	<0.1	5.0	39.0	20.o	8.0
Calcium	32298	25749	37094	31999	31419
Cadmium	0.6	0.5	0.7	0.3	0.05
Cobalt	7.1	6.9	6.5	5.1	20.0
Chromium	63.0	54.0	93.0	83.0	241.0
Copper *	12.0	16.0	15.0	10.0	20.0
Iron	7414	11014	10769	9694	23579
Magnesium	7997	7092.1	9217.1	9082.1	18687.1
Manganese	224.0	196.0	146.0	131.0	706.0
Molybdenum	2.6	0.0006	1.0	0.0006	0.0006
Nickel	32.0	27.0	36.0	27.0	119.0
Lead *	42.0	51.0	76.0	57.0	36.0
Vanadium	38.6	34.0	54.0	54.0	92
Zinc	45.0	40.0	74.0	41.0	66.0
Sodium	350	350	7400	3800	5200

* Determined by (AAS)

Table 5. Number of barley seedlings per pot and quantity of irrigation water after 14 days of 1st irrigation

Soil sample Nos. / Date	1	2	3	4	5	irrigation
17/8/2008	0	0	0	0	0	saturation
21/8/2008	1	2	0	0	0	10 ml
24/8/2008	2	4	0	0	o	15 ml
25/8/2008	2	4	0	0	0	5 ml
26/8/2008	2	4	0	0	0	15 ml
28/8/2008	6	8	0	0	0	15 ml
31/8/2008	7	10	0	0	0	

Table 6. Number of barley seedlings per pot in washed polluted soils and quantity of irrigation water after 14 days of 1st irrigation

Soil sample Nos. Date	3	4	5	irrigation
1/9/2008	0	0	0	saturation
/9/20084	1	0	0	10 ml
7/9/2008	4	0	0	15 ml
9/9/2008	5	0	1	15 ml
11/9/2008	5	0	2	15 ml
14/9/2008	5	0	2	15 ml

Table 7. Analysis of the leachates of three consecutive leachings by water for the three soil polluted samples

Sample sample Nos. Date	3			4			5		
Consecutive leaching	1	2	3	1	2	3	1	2	3
E.C dS/m	12.26	7.06	4.22	12.36	5.64	3.17	31.50	14.80	6.50
pH	7.3	7.71	7.80	7.45	7,81	7.83	7.48	7.81	8.11
Total alkalinity m mol$_c$ L^{-1}	0.51	0.54	0.56	0.54	0.54	0.59	0.49	0.81	1.35

petroleum products seems to prohibit the germination of barley seeds. Such an effect was reduced drastically after several washings by water for some polluted soils, while in some other samples no effect could occur due to washing, indicting that there are some components need to be examined to verify, what are perhaps other constituents of petroleum products, that would be of probable risk in germination of seeds sown in soil polluted with these products.

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