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Soil Contamination by Crude Oil

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THE EXTENT of pollution from crude oil in sandy soil at different distances from oil well at Ras Sudr (South Sinai) was determined. Total petroleum hydrocarbons (TPH) represents 82.8 % of the studied crude oil. The studied crude oil contains one basic hydrocarbon, paraffins (C_{11} to C_{32}). Fe and Mn are importantly present in large concentrations while Cd and Cu are found in low concentrations.

Heavy metals concentrations in the soil showed a horizontal distribution with tendency to decrease with increasing the distance from oil well. The largest concentrations were found at 50 m distance as the average concentrations were 6.9 , 63 , 120 , 23.6 , 649 and 8563 $\mu g g^{-1}$ for Cd , Pb, Zn , Cu , Mn and Fe, respectively. For the six heavy metals except for Cu, significant differences between the three transects (50 , 200 , and 800 m) were found. Cd showed the largest variation while Mn and Fe showed the lowest variations with distance.

TPH concentration increased in soils near the well. The soils located in the vicinity of the oil well (50 and 200 m) are heavily polluted areas (> 200 $\mu g\ g^{-1}$). The soils at 800 meters from the oil well are moderately polluted (50-200 $\mu g\ g^{-1}$) as they contain 142.9 $\mu g\ g^{-1}$.

Keywords: Crude oil, Sandy soil, Contamination hydrocarbons, Heavy metals.

Crude oil is extracted world wide of more than 65 million barrels per day which meet the bulk of the world's energy requirements. However, it is a potential hazard and can cause severe and lasting damage if it accidentally discharged into the environment. Such accidents happen despite the fact that distribution and storage network for crude oil is closely monitored.

In the last 20 years, there has been considerable researches on the fate and effects of petroleum in environment. Investigations into the effects of crude oil on plants have concentrated on the direct toxic effects of oil on the upper part of plants (Baker, 1970; De Jong, 1980 and Anoliefo & Vwioko, 1995). However, little is known about the effect of oil on the soil and its micro-organisms.

Crude oil contains many organic compounds which is rich in heavy metals (Clark & Brown, 1977; Literathy *et al.*, 1992, and Koronelli, 1996) and water soluble hydrocarbons (Clark & Brown, 1977; Butt *et al.*, 1985; Jenifer *et al.*, 1993 and Koronelli, 1996).

Most of the oil wells in Egypt are situated in desert, unfortunately, near the promising areas for agriculture expansion. There is a need for monitoring levels of oil contaminants. Therefore, the present study was undertaken to determine the extent of pollutants from crude oil in the soil at different distances from the oil well at Ras Sudr, South Sinai, Egypt.

Material and Methods

A sandy soil from Ras-Sudr, south Sinai, Egypt near by a petroleum well was used in this study. Soil samples were taken at 50 (D_1), 200 (D_2) and 800 (D_3) meters distance from the oil well in circles surrounding the oil well. Five soil samples were collected from each circle distance at three depths (0 - 15, 15 - 40 and 40 - 60 cm). The 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%. The physical and chemical properties of the studied soil samples were determined according to Jackson (1967); Piper (1950) and Tucker (1971). Total content of Cd, Pb, Fe, Mn, Zn and Cu 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 kilometers from Ras-Sudr Agricultural Experimental Station of the Desert Research Center, South Sinai, Egypt.

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). Hydrocarbons of the oil were extracted according to the method described by Farag *et al.* (1990) using hexane and the solvent evaporated under vacuum. Hydrocarbons were determined using GLC apparatus (GLC pyeunicam pa 4550 capillary chromatography).

Results and Discussion

Properties of the crude oil

The studied oil, represents a complex mixture of both organic and inorganic components. Trace metals are one group amongst the inorganic component present in the crude. Fe and Mn are importantly present in greater concentration while Cd and Cu are found in low concentrations. The concentrations of Fe, Mn, Zn, Pb, Cu and Cd in crude oil are 8960, 462, 95.0, 37.0 14.3 and 6.0 $\mu g\ g^{-1}$, respectively (Table 1).

The hydrocarbon groups are mixtures of components with various carbon structures as shown in Table 1 and Fig.1. Total petroleum hydrocarbons (TPH) represent 82.82 % of the crude oil. The studied crude oil contains one basic hydrocarbon, paraffins C_{11} to C_{32}. Twelve various hydrocarbons are found in the studied crude oil (Table 1). Triacontane (C_{30}) represents the greatest percentage of the crude oil (46.04 %) followed by octacpsane (C_{28}) 10.08 % while dodecane (C_{12}) represents the lowest one (0.85%).

Soil pollution by crude oil

Heavy metals

Heavy metals concentrations showed a horizontal distribution with tendency to decrease with increasing the distance from oil well at all directions in the studied area (Fig. 2). The greatest concentrations were found in transect D1 (50 m distance), as the average concentrations were 6.9, 63, 120, 22.6, 649 and 8563 $\mu g\ g^{-1}$ for Cd, Pb, Zn, Cu, Mn and Fe, respectively.

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

a – Heavy metals ($\mu g\ g^{-1}$).

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

For concentrations of the examined heavy metals, except for Cu, significant differences between the three transects were observed (Table 2). Cu showed only significant differences at transect D2 (200 m). These results suggested that the processes of drilling and extraction of crude oil from underground stores in the oil field resulted in heavy metals contamination from crude oil. A common feature is the longitudinal gradient for all metals, with greater values near the oil well and lowest ones for the samples far from the well. These distribution suggested that the studied elements distributions are being controlled to a large extent by the closeness to the source of oil.

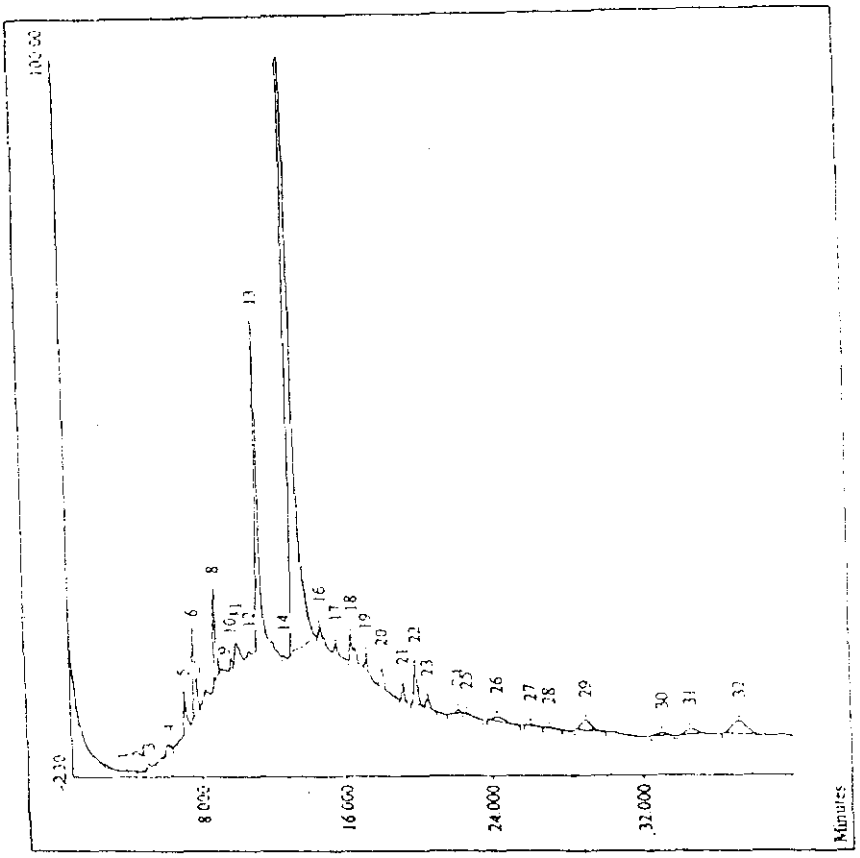

Fig. 1. Gas chromatogram of the studied crude oil from petroleum well at Ras-Sudr.

Total concentration of Cd ranged between 1.1-7.2 μg g^{-1}, with an average of 6.9 μg g^{-1} in transect D_1 and 1.6 μg g^{-1} in transect D_3. Cd is the element that showed the greatest variation in the studied polluted soils (ratio of maximum/minimum values is 5.75).

Total Pb increased in soil samples beside oil well. The average total value for lead is 63 μg g^{-1} with a maximum of 63 μg g^{-1} at D_1 and a minimum of 23 μg g^{-1} at transect D_3. Pb showed the second greatest variation (ratio of maximum/minimum values is 3.2).

Cu concentrations varied from 7 to 22 μg g^{-1}, with an average of 22.6, 14.4 and 12.2 μg g^{-1} at transect D_1, D_2 and D_3, receptively. The average value for zinc is 88.5 μg g^{-1} with a maximum of 120 μg g^{-1} and a minimum of 57 μg g^{-1} at D_3 transect.

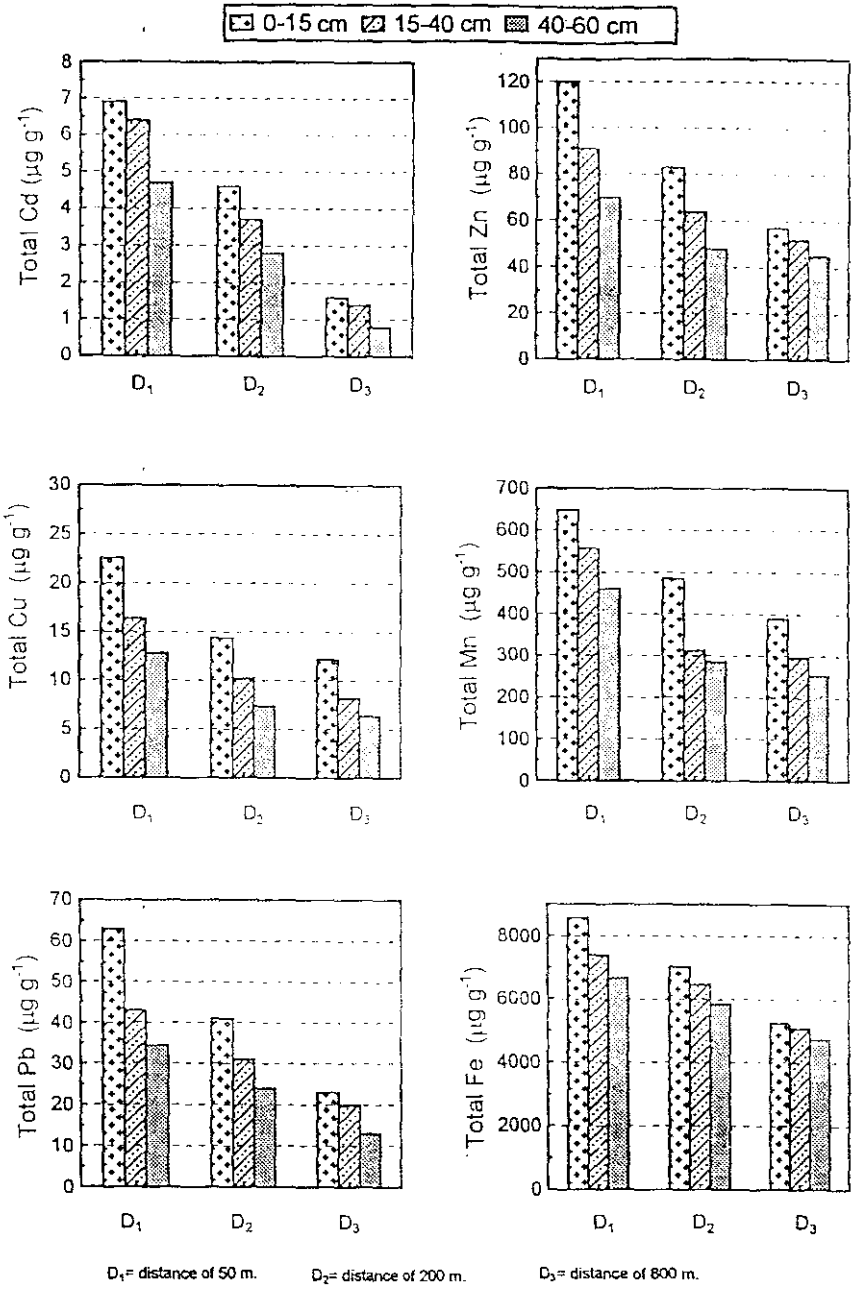

Fig. 2. Average total concentrations of Cd, Cu, Pb, Zn, Mn, and Fe in soil samples at different distances from oil well.

TABLE 2. Least significant difference for heavy metals at different distances.

Distances	Means of total heavy metals (ppm)					
	Cd	Pb	Zn	Cu	Fe	Mn
D1	6.92 a	63.2 a	120.4 a	22.6 a	8563 a	648.8 a
D2	4.62 b	41.0 b	82.8 b	14.4 b	7030 b	485.2 b
D3	1.64 c	22.6 c	56.8 c	12.2 b	5242 c	390.2 c
L.S.D	0.30	5.87	7.33	3.82	1003	75.7

Mn and Fe are found to be the elements of the smallest variations with distance from oil well, (the ratio of maximum/minimum values is 1.8 and 2.01, for Mn and Fe, respectively). They also showed the greatest concentrations among the studied elements. The average total concentrations are for Fe 8563, 7030 and 5242 μg g^{-1}, and for Mn 649, 485, and 390 μg g^{-1} at D_1, D_2 and D_3 transect, respectively.

Heavy metals concentrations showed also a vertical distribution with a tendency to decrease with soil depth in all the studied sites (Fig. 3). The surface layer (0-15 cm) showed the greatest concentrations, *i.e.*, 6.9, 67, 126, 27, 649, and 9170 μg g^{-1} for Cd, Pb, Zn, Cu, Mn and Fe, respectively. The percent decrease in Cd, Pb, Zn, Cu, Mn, and Fe concentration with depth is about 92, 68, 75, 72, 85 and 86 % at 15-40 cm soil depth; and 68, 54, 58, 56, 71, and 77 % at 40-60 cm soil depth for the aformentioned elements, respectively.

Hydrocarbons

The greatest total petroleum hydrocarbons (TPH) concentration (320μg g^{-1}) is recorded in the soil collected near the oil well, *i.e.*, transect D_1, 50 m from oil well. This is thought to be due to transportation of these pollutants from their original points, indicating direct petroleum input in the soils located in the vicinity of the oil well. Total petroleum hydrocarbons concentrations in the area far from oil well (D_3, 800 meters) is 142.9 μg g^{-1} which comes to be about 50% that of D_1 (Table 3).

TABLE 3. Concentration of petroleum hydrocarbons (μg g^{-1}) of surface soil samples (0-15 cm) at different distances from oil well.

Compounds		Distance from oil well (meter)		
		D1 (50)	D2(200)	D3 (800)
Dodecane	C_{12}	7.2	4.0	1.2
Trtradecane	C_{14}	11.4	8.3	1.7
Hexadecane	C_{16}	18.6	13.0	3.6
Octadecane	C_{18}	20.4	19.6	14.0
Eicosane	C_{20}	18.4	13.2	11.4
Docosane	C_{22}	29.1	21.5	16.8
Teracosane	C_{24}	21.2	18.4	5.2
Hexacosane	C_{26}	15.7	12.3	3.7
Octacpane	C_{28}	48.5	36.0	21.8
Triacontane	C_{30}	71.6	54.2	27.0
Squalane	C_{31}	40.2	27.6	24.5
Dotriacontane	C_{32}	18.0	15.4	12.0
Total		320.2	243.5	142.9

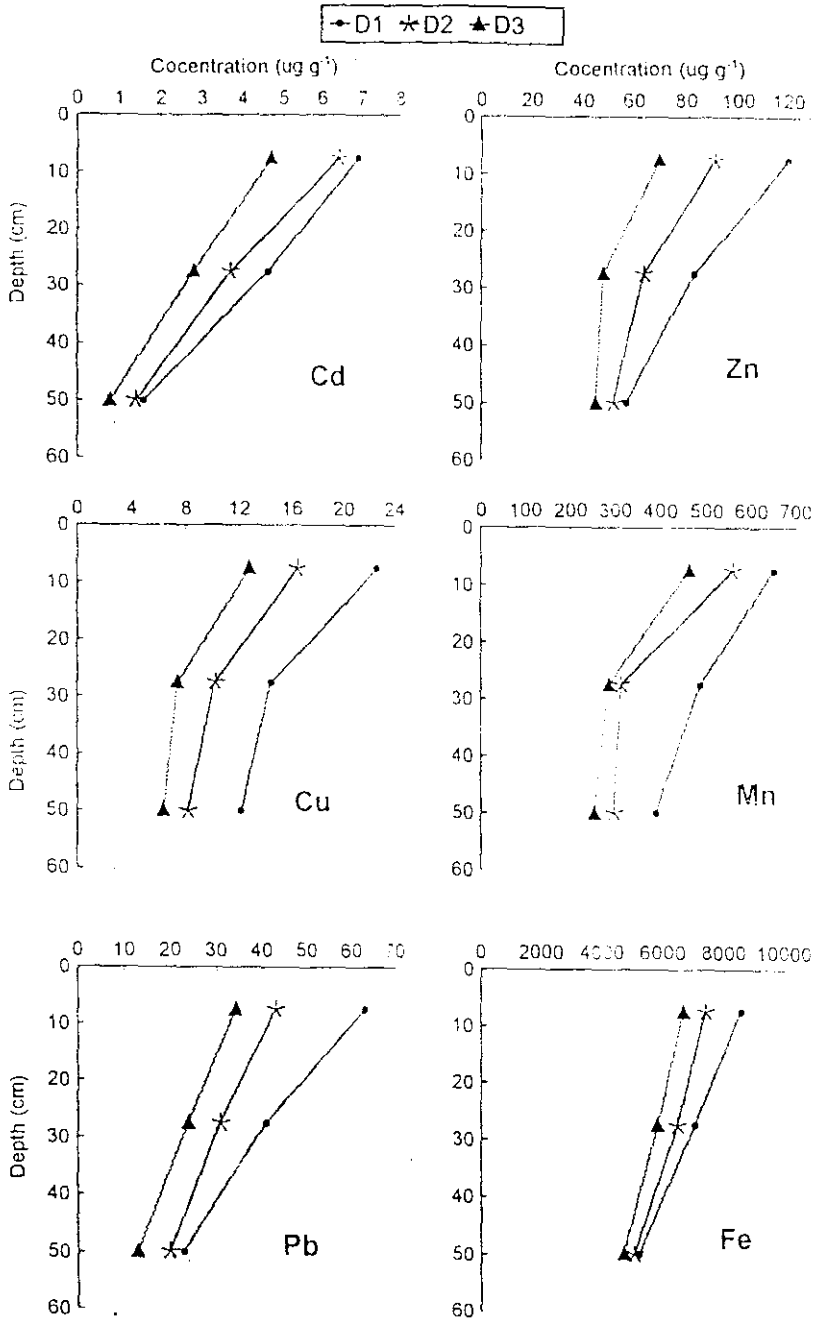

Fig. 3. Heavy metals concentration as affected by soil depth at different distances from oil well.

Bearing in mind the study of Literathy *et al.* (1992), who suggested TPH values as guidelines for pollution in sediments. Accordingly to his criteria, the soils located in the vicinity of the oil well 50 m distance (D_1) and 200 m distance (D_2) are heavily polluted soil (>200 $\mu g\ g^{-1}$) and the soils at distance of 800 m (D_3) are moderately polluted (50-200$\mu g\ g^{-1}$).

Triacontane C_{30} consists the greatest concentration of the crude components 71.6, 54.2 and 27 $\mu g\ g^{-1}$ in transect D_1, D_2 and D_3, respectively, while dodecane C_{12} represents the lowest concentrations 7.2, 4.0 and 1.2 $\mu g\ g^{-1}$, respectively (Table 3). However, the distribution concentrations of the various hydrocarbons in the studied soils are similar to that of the crude oil, confirming that the crude oil from oil well is the main source of pollutants.

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تلوث التربة بزيت البترول

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تم دراسة التلوث من بئر للبترول فى منطقة رأس سدر جنوب سيناء على الأراضى الرملية الموجودة على مسافات مختلفة من البئر. وبينت الدراسة أن الهيدروكربونات تمثل ٨٢,٨ % من البترول المستخدم وأنها كلها من البارافينات (C_{11} to C_{32}) . كما أوضحت الدراسة زيادة محتوى البترول من Fe, Mn التى وجدت بتركيزات عالية بينما تواجد Cd, Cu بتركيزات منخفضة.

وأشارت الدراسة إلى وجود توزيع أفقى للعناصر الثقيلة فى التربة حيث يقل تركيزها بالبعد عن البئر. وكان أعلى تركيز على بعد ٥٠ متر من البئر حيث وصلت تركيزات العناصر الثقيلة إلى ٦,٩ ، ٦٣ ، ١٢٠ ، ٢٣,٦ ، ٦٤٩ ، ٨٥٦٣ جزء فى المليون لعناصر Fe, Mn, Cu, Zn, Pb , Cd على الترتيب. ولقد أظهرت النتائج وجود إختلافات معنوية لتركيز هذه العناصر (ماعدا Cu) بين الأراضى المأخوذة على مسافات مختلفة من البئر (٥٠ ، ٢٠٠ ، ٨٠٠ متر). وأظهر عنصر Cd أعلى التغيرات بينما أظهرت عناصر Mn, Fe أقل التغيرات مع البعد من البئر.

وأظهرت الدراسة زيادة تركيز الهيدروكربونات البترولية الكلية بالقرب من البئر حيث وصلت إلى أكثر من ٢٠٠ ميكروجرام / جرام على بعد ٥٠ متر وأعتبرت الأراضى شديدة التلوث ، بينما كانت ما بين ١٤٢,٩ ميكروجرام / جرام على بعد ٨٠٠ وأعتبرت أراضى متوسطة التلوث.