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Crude Oil Spillage and the Impact of Drilling Processes on the Soil at Rumaila Oil Field- Southern Iraq

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Abstract

The demand on energy sources throughout the world have led to an increase in the production processes of crude oil which is considered to be the main source of energy, without considering the impact on the environment. The objective of this study is to evaluate the environmental impact of drilling processes and crude oil spillage on soil in the Rumaila oil field, Basra, Southern Iraq. An investigation was undertaken to determine the content of Polycyclic Aromatic Hydrocarbons (PAHs) and heavy metals in the soil. Ten soil samples were collected near oil wells and analyzed. The results showed a high concentration of PAHsin the soil, particularly (Acenaphthene, Fluorene, Anthracene, Fluoranthene and Pyrene) due to crude oil spillage. The heavy metals content (i.e. As, Co, Cr, Cu, Fe, Ni, Pb, V and Zn) and (B) of the analysed soil samples were compared with one standard soil sample taken from an urban area far from the pollution sources as a background. High concentrations of Co, Cr, Ni, Pb, V and B were observed in all soil samples, and therefore, exceeded the international standard limits in soil. This study documented high concentration of PAHs and heavy metals in the chosen area.

Keywords: PAHs, Rumaila Oil Field, Crude oil, Heavy metals, Drilling processes.

انسكاب النفط الخام و اثر عمليات الحفر في التربة في حقول الرميلة النفطية – جنوب العراق

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الخلاصة

الطلب على مصادر الطاقة على مستوى العالم أدى الى زيادة في إنتاج النفط الخام و الذي يعد مصدرا رئيسا للطاقة، وعدم الأخذ بنظر الاعتبار اثر عمليات الإنتاج على البيئة. الهدف من الدراسة الحالية هو تقييم الأثر البيئي لعمليات الحفر و انسكاب النفط الخام على التربة في حقل الرميلة النفطي في محافظة البصرة جنوب العراق. أجريت تحريات لتحديد المركبات الاروماتية العطرية و العناصر الثقيلة في التربة. جمعت 10 عينات من التربة بالقرب من الآبار النفطية و تم تحليلها. أوضحت النتائج وجود تركيز عالي من المواد الاروماتية في عينات التربة، و خاصة مركبات(الاسينافسين، الفلورين، الانثراسين، الفلورنثين و البيرين) بسبب انسكاب النفط الخام أثناء عمليات الحفر. محتوى العناصر الثقيلة في عينات التربة التي حللت تمت مقارنتها مع عينة تربة أخذت من منطقة بعيدة عن مصادر التلوث، لوحظ وجود تركيز عالٍ من (الكوبلت، الكروم، الرصاص، الفناديوم و البورون) في جميع عينات التربة بالتالي تجاوزت المحددات العالمية في التربة. سجلت الدراسة الحالية تركيز عالٍ من المواد الاروماتية و العناصر الثقيلة في المنطقة المختارة.

الكلمات المفتاحية: المواد الاروماتية العطرية، حقل الرميلة النفطي، النفط الخام، العناصر الثقيلة و عملية الحفر.

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Introduction:

One of the major causes of environmental pollution is oil spillages, which refers to the accidental leakage of crude oil or refined products on to land,as a result of the process of the production and distribution of crude oil. The demand for crude oil as a source of energy has caused a dramaticincrease in its production, transportation and refinery, resulting in environmental pollution. Oil spillages occur in different parts of the world, causing serious hazards to the environment [1].Oil excavation, production and transport activities present a risk of accidental oil spills with potential consequences to the environment [2]. Petroleum hydrocarbon pollution is one of the main environmental problems, not only because of the significant amounts released, but also due to their toxicity [3].

Crude oil represents a complex mixture containing both organic and inorganic chemical species, trace metals being one group of the inorganic components present in this type of matrix [4].The significance of petroleum and natural gas in the modern world is well known. Nevertheless, many sites within the oil industryhave become contaminated due to activities characteristic to this business, for instance, oil exploration and production, refining, and spillage of drilling fluids and crude oil. These activities have led to the releaseof various organic and inorganic pollutants into the soil, air, and water, including trace elements, heavy metals and PAHs [5].The increase of heavy metals in the soil in oil fields has been largely caused by crude oil spillage [6,3].

PAHs are consideredto be one group of organic components and are associated with oil spills that are of great concern due to their toxicity, mutagenicity, carcinogenicity and persistency [7,8].The sources of PAHs in soils can come from raw materials,which contain them such as resins and oils, black carbon asphalt, etc. [9,10].

A number of PAHs are mutagenic and carcinogenic [11-13].The accumulation of PAHs in soils leads to contamination of groundwater via leakages from the soil [14-16]. In addition, PAHs may also be directly or indirectly transmitted from soil into terrestrial food chains, resulting in the exposure of humans and other living organisms to PAHs [17,16].

The study area is a part of the Basra governorate, the centre of the oil industry in Iraq. It islocated in the south- east part of Iraq Figure 1. The Basra governorate covers approximately (19070) km^2. It is considered to be the third largest city in area and population, in Iraq. It is bordered by Iran from the east and Kuwait from the south. It contains the main oil field in Iraq and the Rumaila oil field is part of the main field, which is located to the west of the Basra governorate. It includes several oil installations such as Al-Shaieba refinery and the extraction of crude oil from the southern and northern Rumaila oil field. To the north of Basra City, the Tigris River meets the EuphratesRiver in “Garmat Ali” forming the Shatt Al-Arab waterway with a length of 190 km to its outlets in the Arabian Gulf. The study area is located to the north of Safwan- Zubair area, which is considered as the main area for the cultivation of different types of vegetables that the Basra governorate depends on.

The aim of this work is to measure PAHs and heavy metals in the soil near oil wells inthe Rumaila oil field in southern Iraq. The observation of the levels and distributionof PAHs and heavy metals in the soil is an important aspect, in order to evaluate the potential health effects. As the data on PAHs in Iraqi’s soil,particularly Basra City soil is restricted; this is the first study thataims to reportthe concentrations of PAHs in Iraqi soil.

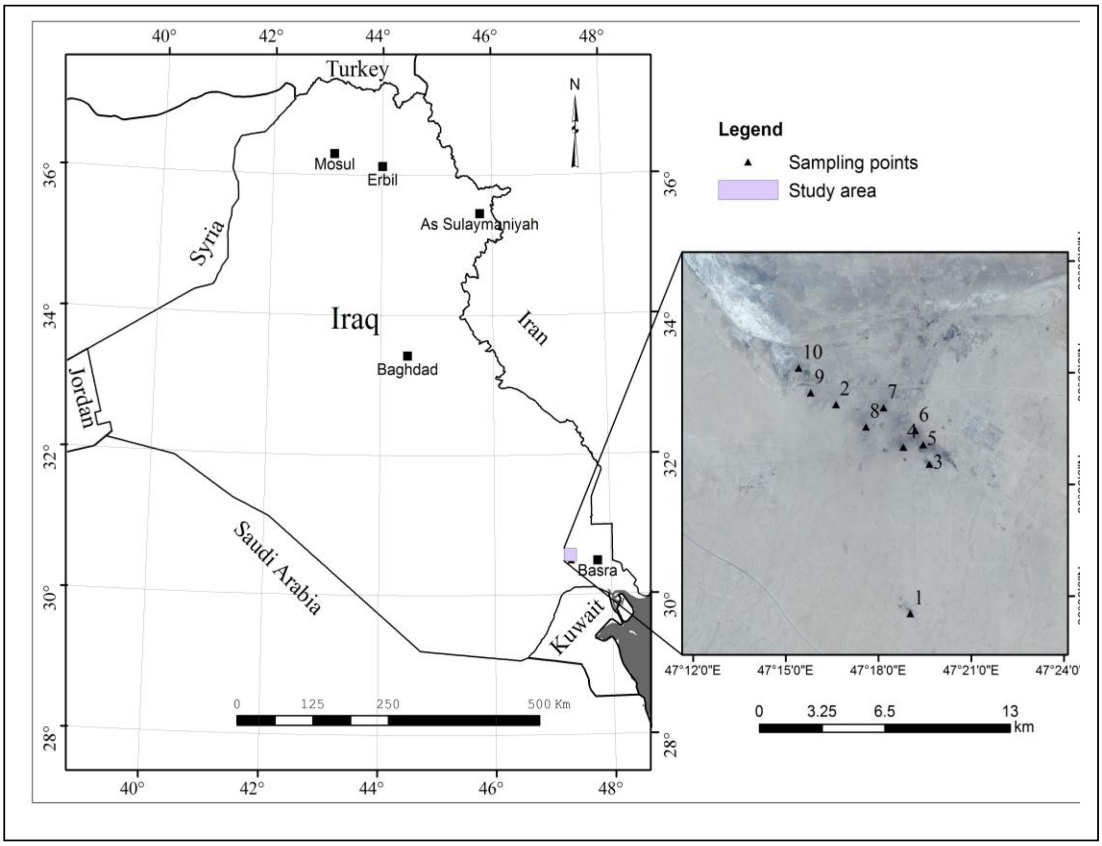

Figure 1- Location map showing Rumaila oil field (The Area of Study) and sampling points

Geological setting:

The study area is characterized by poor rock exposure due to low relief and a considerable cover of quaternary deposits. Jabal Sanam is the only visible structure in the study area; it is a unique domal structure penetrated in Al-Batin fan sediments with a relative height of (110 m), has structural origin and is considered (most probably) to be a salt dome [18]. The most important geological formations in the studied area are:

1. The Dibdibba Formation **(**upper Miocene- Pliocene- Pleistocene).The age of this formation was estimated by[19] as upper Miocene- Pliocene- Pleistocene. However, a recent investigation shows that the Pleistocene part belongs to the alluvial fan of Wadi Al-Batin. The formation is partly exposed on the eastern and southern side of Jabal Sanam, while the rock types indicate that the formation is of a fluvial origin. No fossils have been recorded [20].
2. The Zahra Formation **(**Pliocene- Pleistocene). The sequence of green calcareous sandstone (1.8 m), brown claystone (1.2 m) and recrystallised limestone (1.2- 1.7 m) at the top of small scattered isolated stony hills is considered to be the Zahra formation, which is exposed in the north western corner of the study area, and [21] have considered the brown claystone and sandstone.

Materials and Methods:

Sampling:

The sampling process was conducted in Rumaila oil field by collecting ten contaminated soil samples with crude oil spillage and drilling fluids taken from neighbouring soil of oil wells, soil samples were compared with one standard soil sample taken from an urban area((Tannumah area) east of Basrah City) far from the pollution sources as a background Figure-2. The soils were air-dried, homogenized with a pestle and mortar and passed through a 2mm sieve prior to extraction.

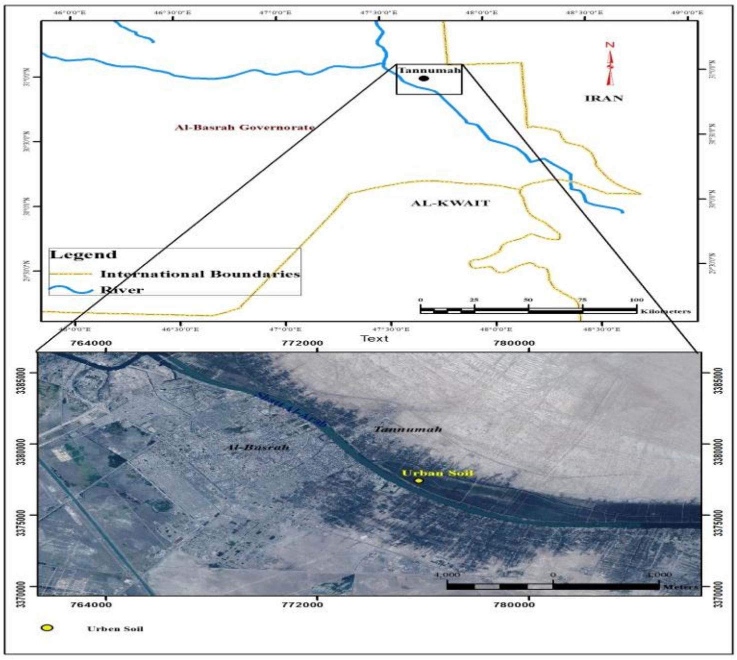

Figure 2-Urban soil sample (Tannumah Area) east of Basrah City

Chemicals:

The chemicals used were acetone, iso-hexane (HPLC grade; Fisher Scientific, UK) and QTM PAH Mix which contains Acenaphthene, Acenaphthylene, Anthracene, Benzo (a) anthracene, Benzo (a) pyrene, Benzo (b) fluoranthene, Benzo (g,h,i) perylene, Chrysene, Dibenz (a,h) anthracene, Fluoranthene, Fluorene, Indeno (1,2,3-cd) pyrene, Naphthalene, Phenanthrene, Pyrene, 2-Bromonaphthalene (2000µg/ml in methylene chloride; Sigma Aldrich, UK).

Soil Extraction:

The chemical extraction method uses mechanical agitation with acetone: hexane mixture (1:1) to extract PAHs from the soil. 1g of dry soil portions wasbriefly sonicated in 10ml of acetone: hexane mixture (1:1 v/v) for 15 minutes, followed by agitation in a rock and roll shaker for an hour at a speed of 60 rotations per minute (rpm). After extraction, 4ml of deionised waterwas added to the separate hexane layer from the acetone layer. Next, 0.5ml of hexane layer was decanted, concentrated to 1ml and eluted with hexane through a column containing 1g of 1:1 deactivated silica and dry sodium sulphate mixture fora cleanup. Finally, the extractswere concentrated again and transferred to auto sampler vials.

PAHs Analyses:

All the extracts were analysed using an Agilent 19091J-133 gas chromatograph equipped with a flame ionization detector (FID), split/splitless injector and a HP-5 silica fused capillary column with dimensions of 30m x 0.25mm x 0.50µm. A split injection (30:1) of 1 µl was automatically inducted. The oven program started with an initial temperature of 100˚C, held for 2 minutes, the temperature was increased by 15˚C to 300˚C and sustained for 5 minutes. Detection was performed using the total ion current (TIC) mode. The quantification of PAHs from soil sampleswas performed using a series of external standards, with concentrations 0.1; 0.5; 1; 5; 10 µg/ml, dissolved in iso-hexane.

Heavy Metals:

Nine heavy metals and Boron (As, Co, Cr, Cu, Fe, Ni, Pb, V&Zn) and (B) were analysed using ICP-MS technique at the University of Freie in Berlin,Germany. The preparation of soil samples to measure the heavy metals and Boron was conducted using the cool digestion methodas follows:

One gram of soil was dried at air temperature, then placed in a beaker (100 ml), after sieving through 50 meshes sieve and suspended in 3:1 of HCL and HNO_3, the mixture was subsequently put on a magnetic stirrer for (24) hours and filteredto be ready for measuring by using the ICP-MS technique.

Results and Discussion:

- Heavy Metals content:

Heavy metals in crude oil find their way into the environment due to spillages. Contamination by heavy metals depends on the toxicity and concentration of each metal in the crude oil. Heavy metals enter petroleum very early in its formation from source rocks, mainly as organometallic complexes, especially metalloporphyrins, which are very stable [22-24]. There are other sources of trace metals in crude oils, which include minerals leaked during migration and contamination during production [25].High concentrations of metals in soil can be harmful to the ground, upsetting the delicate ecological balance and contaminating food sources [26,24].

The heavy metals in this study were discovered in different proportions and their content in soil samples are given in Table 1. The results show high concentrations of some heavy metals Figure-3.
B varied from (5 to 15 ppm) with a mean of 9 ppm Table-1, whilstthe as concentration ranges from (4.5 to 6.5 ppm) with a mean of 5.6 ppm. Co, Fe and Zn varied from (4, 4080, 36 to 15, 34200, 55 ppm) with a mean of 7.7, 8012 and 44 respectively, and their mean was less than their mean in some Iraqi soils Table-1. Cr and Cu varied from (133, 12 to 248, 68ppm) with a mean of 179 and 27 respectively Table-1. The Ni concentration in this study was between (20- 114 ppm) with a mean of 53 ppm.The Ni content of crude oils is in the range < 1- 80 ppm [27-29]. Pb exhibited the highest mean (174 ppm) ranging between (141 and 220 ppm), with the increase of Pb concentration in this study due to the petroleum industries and drilling processes in the Basra Governorate [30]. The V concentrations varied from (121 to 300 ppm) with a mean of 159 ppm, and vary widely in concentrationswithin the crude oils (1- 1500 ppm) [31-32].

All the selected soil samples in the studied areaexhibited significantly higher contents,particularly (Cr, Ni, Pb, V and Zn) due to their large concentration in crude oil compared with the concentration of the same metals in the sample taken from urban area, which is far awayfrom the contamination sources (sample 11) Table-1.

Table 1-The status of soil contamination by certain heavy metals

Samples ID	As	B	Co	Cr	Cu	Fe	Ni	Pb	V	Zn
W 1	6.5	15	14	248	68	34200	114	208	200	49
W 2	6	8	15	220	25	5790	57	160	300	46
W 3	5.9	11	5	170	20	5200	55	190	122	55
W 4	5.8	8	11	165	15	5000	62	182	126	40
W 5	5.5	9	5.5	185	26	6090	44	220	121	48
W 6	6	7	5	150	17	4780	42	170	133	36
W 7	4.5	5	4	172	18	4630	45	141	124	39
W 8	4.5	7	4.5	180	29	5170	48	160	123	44
W 9	5.6	12	5	171	42	5180	39	150	142	42
W 10	6	9	8	133	12	4080	20	158	200	41
11	2.8	4.2	5	13	15	1358	20	36	23	19
Mean	5.6	9	7.7	179	27	8012	52.6	173.9	159	44
Average in Iraqi Soils	----	----	19*	162*	17*	22891*	21*	39*	0.8**	113**

*[33] **[34]

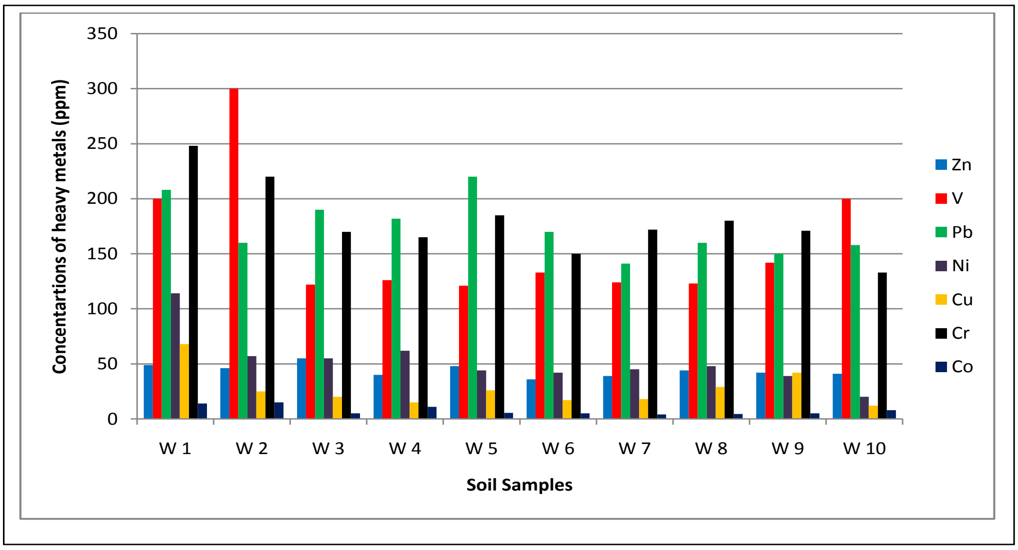

Figure 3-Concentrations of heavy metals in soil samples (ppm)

- Polycyclic Aromatic Hydrocarbons (PAHs)

Many organic chemicals such as PAHs have been reported as high organic contaminants in the main study about marine organisms and sediments [35-39].Crude oil is a complex mixture of hydrocarbons such asPAHs and non-hydrocarbon(s) compounds including heavy metals, which are potentially phytotoxic [40]**.**Airborne PAHs bind to suspended particles and are deposited onto soil and water [41].The PAHs of petrogenic origin, prevalent in coals and crude oils are formed from digenesis of sedimentary organic material under low and moderate temperature and tend to consist of low molecular weight PAHs with two to three rings [42-43].PAHs enter the environment through three main processes, including release of petroleum (main cause in the present work), combustion of organic compounds at a very high temperature and digenetic processes.

Pyrogenic PAHs are formed by incomplete combustion of organic material, whilst the petrogenic PAHs are present in oil and some oil products [44-46]. This fact is clearly presented in Table-3 [47-48]. Naphthalene varied from (2.54 to 4.47 µg/g) with a mean of 3.2 µg/g, whilstAcenaphtylene ranged from (1.24 to 3.64 µg/g)with a mean of 2.3 µg/gTable 2. Acenaphthene varied from (11.31 to 19.28 µg/g) with a mean of 17.7 µg/g, the mean of Fluorene was 16.9µg/gand ranged from (11.44 to 28.53 µg/g). Naphthalene, Acenaphtylene, Acenaphthene and Fluorene concentrations were not found in the soil samples taken from the urban area (sample 11) Table 2. Phenanthrene and Anthracene varied from (8.51, 11.54 to 12.72, 34.37 µg/g) respectively with averages of 9.8, 23.5 µg/g. Fluoranthene ranged from (4.71 to 38.54 µg/g)with a mean of 28.8 µg/g, meanwhile the concentration of Pyrenevaried from (2.50 to 41.30µg/g) with a mean of 31 µg/g Table 2.The phenanthrene, Anthracene, Fluoranthene and Pyrene concentrations were more evident than their concentrations in the samples acquired from the urban area (sample 11), which were (1.89, 1.20, 2.73 and 5.53 µg/g) respectively Table-2.Pyrene, Fluoranthene and Anthracene showed high concentrations Figures-4,-5.

Accordingto Danish standards, the PAHs concentration in unpolluted soils is 0.02–0.05 µg/g [42-49]. All soil samples in the present work have significantly higher concentrations of PAHs that exceeded the standard levels in unpolluted soils Table 2.The results of the PAHs were compared with the soil’s international standard levels as there is no available standard with regards to Iraqi soil.In addition, the drilling processes added high concentrations of PAHs to the neighbouring soils.

Table 2- PAHs (Naphthalene,Acenaphtylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene and Pyrene) status in the soil samples.

Soil Samples No.	Compounds							
	Naphthalene	Acenaphtylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
W1	2.54	1.76	17.59	16.39	7.85	20.41	4.71	2.50
W2	3.30	2.76	18.56	14.10	11.91	34.37	38.54	25.73
W3	2.99	1.91	19.07	18.32	11.98	25.92	35.39	36.83
W4	4.07	3.53	11.31	20.67	12	19.48	27.71	35.42
W5	4.13	3.31	13.12	18.47	11.01	11.54	21.39	39.22
W6	4.47	3.34	12.41	26.62	12.72	31.72	34.75	41.30
W7	4.05	3.64	16.37	28.53	12.45	18.03	35.51	35.30
W8	3.19	1.93	19.28	14.95	9.95	22.40	28.75	34.24
W9	2.82	1.24	12.38	11.44	8.51	33.02	32.12	29.65
W10	----	-----	-----	-----	-----	17.90	29.60	30.51
11	----	----	-----	----	1.89	1.20	2.73	5.53
Mean	3.2	2.3	17.7	16.9	9.8	23.5	28.8	31
Int. Standard in Soil	0.5	0.5	0.5	1	3	1	4	4

Table 3-Minimum, maximum, and mean PAHs content in (48) different crude oils (after [49]).

Crude Oil 48 different crude oils

PAHs Minimum mg/ kg	Maximum mg/ kg	Mean mg/ kg
Naphthalene1.2	3700	427
Acenaphthene 0	58	11.1
Acenaphthylene 0	0	0
Fluorene1.4	380	70.34
Anthracene 0	17	4.3
Phenanthrene 0	400	146
Fluoranthene 0	15	1.98
Pyrene 0	9.2	-
Benzo[a]anthracene 0	16	2.88
Chrysene 4	120	30.36
Benzo[b]Fluoranthene0	14	4.08
Benzo[k]fluoranthene 0	1.3	0.07
Benzo[a]Pyrene0	7.7	1.5
Dibenz[a,h]anthracene 0	7.7	1.25
Benzo[g,h,j]perylene 0	1.7	0.08
Indeno(1,2,3-cd) pyrenec 0	1.7	0.08

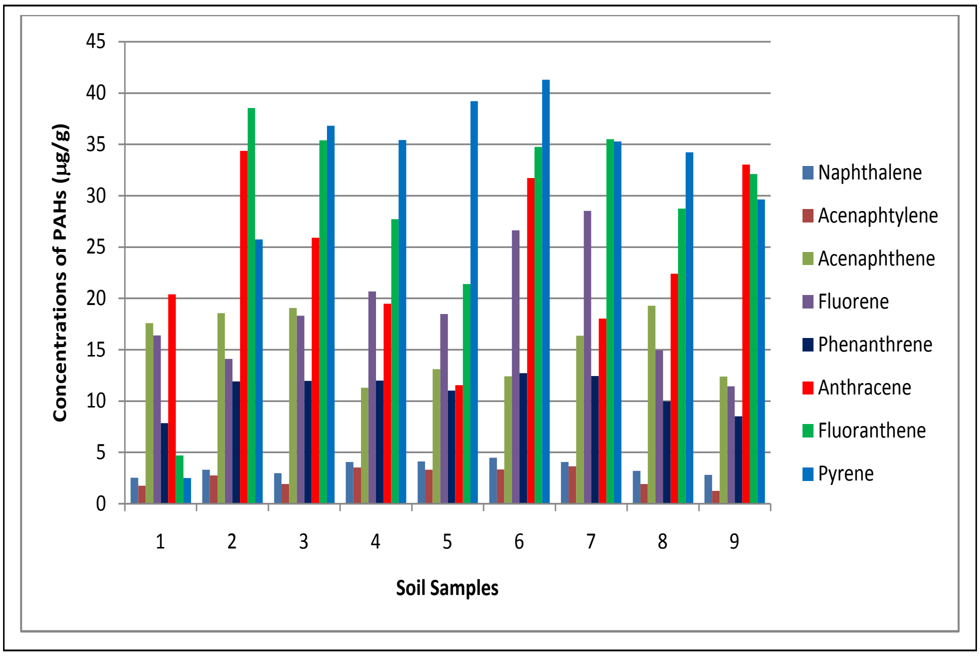

Figure 4- PAHs in the soil samples

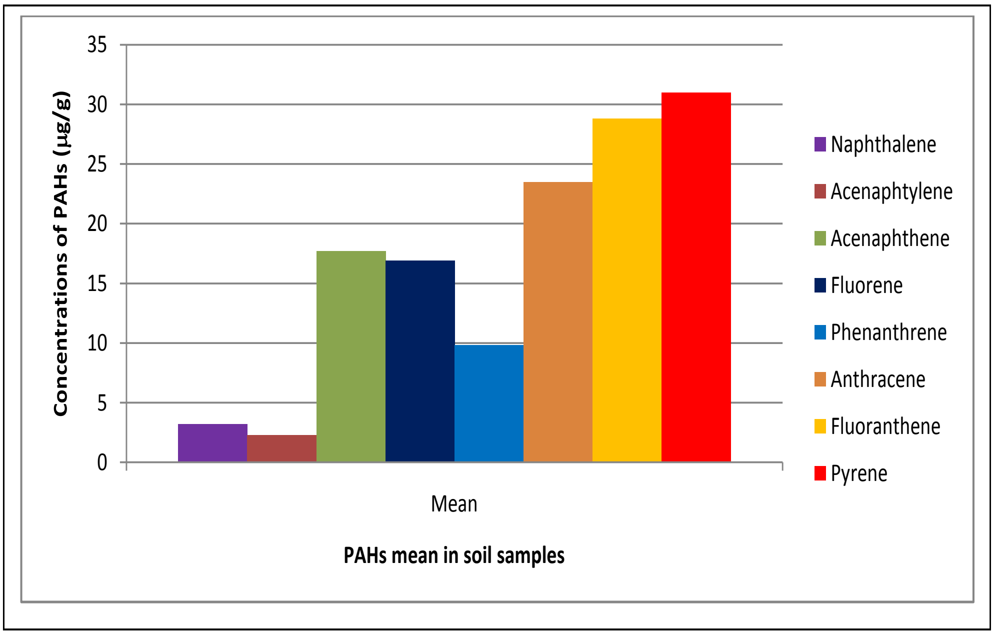

Figure 5-Mean of PAHs in the soil samples

- Correlation Coefficient for the PAHs results:

A correlation coefficient test was conducted using R software on the data obtained from ten sites Table-2. The data is significant at the 0.01 level. (Acenaphthylene, Naphthalene and Acenaphthene) has a moderate positive relationship with Pyrene and in addition, are significantly correlated with the other variables Figure-6. Fluorene and Phenanthrene have a moderate positive relationship with Pyrene and Fluoranthene, and are significantly correlated with the other variables. Pyrene has a strong positive linear relationship with (Fluoranthene, Anthracene) and a moderate positive relationship with other variables and Anthracene has a strong positive relationship with all the variables. Fluoranthene has a moderate positive relationship with (Naphthalene, Phenanthrene and Fluorene) and is significantly correlated with (Acenaphthylene, Anthracene and Acenaphthene).

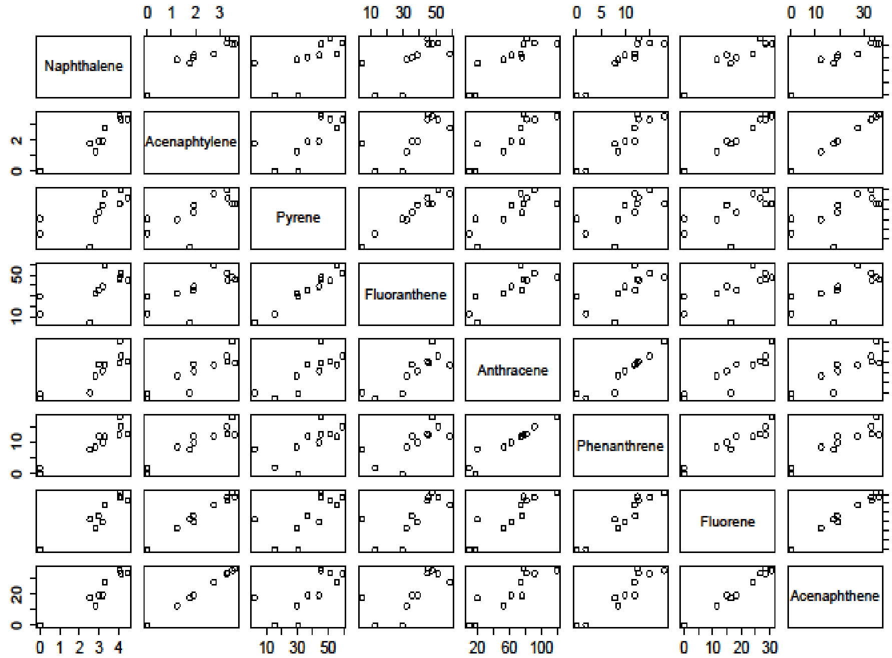

Figure 6-PAHs Correlation scattered plot

- Correlation Coefficient for heavy metals results:

A correlation coefficient performed on the data of heavy metals, Table 1. The data is significant at the 0.01 level. Zn has a weak positive relationship with (V, Ni, Fe, Cu, Cr, Co and As) and has a moderate positive linear relationship with (Pb and B). V has a weak negative linear relationship with Pb and is significantly correlated with Co and moreover, there is a weak positive linear relationship between V and other variables. Pb has a moderate positive relationship with (Zn, Ni, B, As) and a weak positive linear relationship with other elements. Ni is strongly correlated with (Fe, Cu, Cr, As) and moderately correlated with (Pb, Co, B) and has a weak positive linear relationship with (Zn, V). Fe has a weak positive correlation with (Zn, Cu, Pb), a moderate relationship with Co and is strongly correlated with (Ni, Cu, Cr, B, As). Cu is strongly correlated with (Fe, Ni, Cr, B), and has a moderate positive relationship with As, although additionally it has a weak positive relationship with other variables. Cr has a weak positive relationship with (Zn, V, Pb, B), moderate positive relationship with (Co, As) and is significantly correlated with (Fe, Ni, Cu). Co has a weak positive relationship with B. As is strongly correlated with B and has a moderately positive relationship with Co.Figure7shows the relationship between the heavy metals that were studied and their concentrations. The box-and-whisker in this figure indicates that 50% of the studied heavy metals are above the middle of the data bases in (Co, Cr, Ni, Pb, V), 50% of the concentrations of (Cu, As) are above the median of the values, whilst 90% of the values of (Co, V) are above the median of the values.

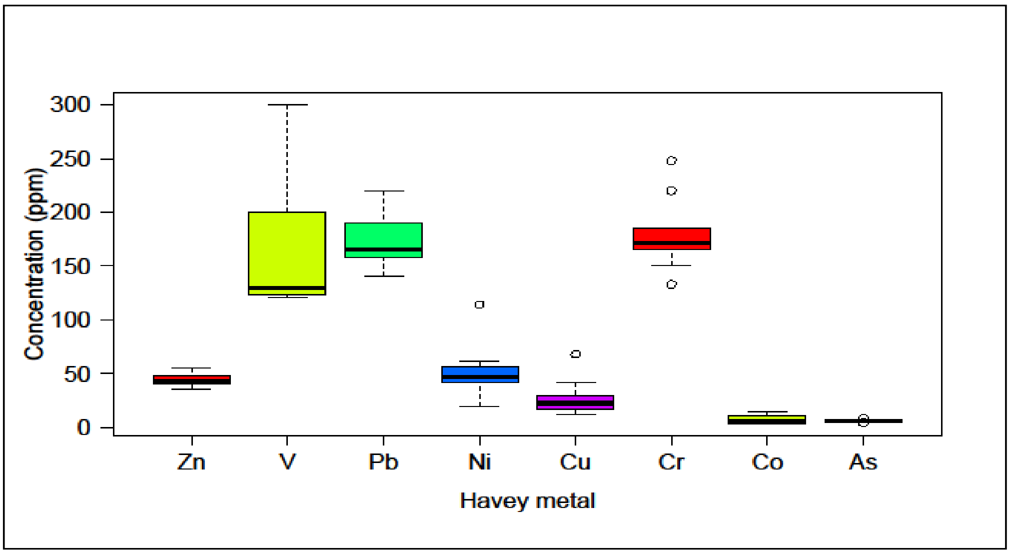

Figure 7- Box-and- whisker plot of heavy metals concentrations

Conclusion

The results showed that drilling processes and crude oil spills inthe Rumaila oil field have addedseveral chemical components to the soil. It is clear that contaminated soil samples contain high levels of PAHs and heavy metals due to the high levels in the crude oil, and that these components can be transmitted to the neighbouring soil as a result of the drilling processes and oil exploration.The prevailing winds maytransfer the contaminants from the oil industry area to a nearby important cultivation area that the Basra governorate depend on. The study area has a high concentration of PAHs, particularly (Acenaphthene, Fluorene, Anthracene, Fluoranthene and Pyrene) due to high concentrations of crude oil, Furthermore, high concentrations of Co, Cr, Ni, Pb, V and B have been observed in all soil samples,which exceeds the international standard limits in soil. The present study documented the high concentrations of PAHs and heavy metals in this area.

It is incumbent upon environmental organizations and those interested in environmental affairs to recognise that substantial background amounts of PAHs and metals which exist in the soil in oil fields,and that they must be responsible for cleaning up these sites to maintain anuncontaminated environment for people and future generations.

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