

## Levels of Polycyclic Aromatic Hydrocarbon (PAHs) in Jordanian oil shale

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### Abstract

The levels of thirteen polycyclic aromatic hydrocarbons (PAHs) were determined in oil shale samples collected from the major deposit sites in Jordan. All analysis were ranged between 92.49 µg/kg (Jurf Ed Drawish) and 2178.03 µg/kg (Wadi Issal). Recoveries of PAHs were found between 72 and 100% and Precision of the method calculated as relative standard deviation (RSD) was ranged between 0.6 and 7%. The limits of detection were between 7 and 70 µg/kg. The total estimated cancer risks of exposure to PAHs in the Jordanian oil shale were ranged from  $2.54 \times 10^{-5}$  to  $5.25 \times 10^{-7}$ . By multiplying these numbers of cancer risks of exposure to soil sample-PAHs by  $10^6$ , it is possible to determine the maximum theoretical number of cancer cases per million of people. The maximum estimated cancer risks cases determined in this study (25 out of million) are well within the acceptable range of excess cancer risk specified by the US Environmental Protection Agency.

**Key Words:** Cancer risk, PAHs, oil shale, Jordan.

### 1. Introduction

Jordan possesses a very large energy resource in its vast reserves of oil shale and it ranked at the 8th position in the world for its shale oil reserves (Alali *et al.*, 2006). There are twenty four known surface, near-surface and deep deposits of oil shale occurrences which have been reported in most of the Jordanian districts. The major deposits of commercial interest for surface mining are located south of Amman in central Jordan in places, such as El-lajjoun, Sultani and Jurf el Darawish (Hamarneh, 1998).

Jordanian oil shale consists of kerogen-rich bituminous limestone and calcareous marls whose color varies within brown, gray or dark-gray and become typical bluish light to gray when weathered. Its kerogen originates from the fossil remains of micro plants and algae accumulated in the seas and lakes that covered most of Jordan some 80 million years ago (Bsieso, 2003).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants derived from the incomplete combustion of organic materials, e.g. any kind of fossil fuels including oil shale. Due to carcinogenic and mutagenic activities of many representatives of this group of compounds, PAHs pollution has become a serious environmental problem. That is why the concentration of PAHs in all compartments of the environment, i.e., water, soil and air, is regulated in most countries of the world (Jao *et al.*, 2009).

A vast literature is available on the chemical analysis of soil, solid wastes from coal combustion and oil shale processing residues, whereas there is a lack of data concerning the analysis of oil shale as it is on polycyclic aromatic hydrocarbons due the potential carcinogenic and mutagenic activity of many representatives of this group of compounds (Viau *et al.*, 2000). Also there is a necessity for Environmental Risk Assessment studies, data concerning the concentration of these pollutants in the environment. Risk assessment can be evaluated by incremental lifetime cancer risk (ILCR) associated with exposures to PAHs in soil samples using the US EPA standard models. The cancer risk was assessed based on exposure according to type of land over the entire lifetime (Chen *et al.*, 2006; USEPA, 1991; Wang, 2007).

## 2. Experimental

### 2.1 Chemicals and Reagents

A standard mixture of PAHs containing the following thirteen compounds: Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Pyrene, Benzo(a) - anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo-(a)pyrene, Indeno(1,2,3-cd)- Pyrene, Dibenzo(a,h) anthracene and Benzo(g,h, i)perylene was purchased from Supleco (USA).

The internal standards 1-Fluoronaphthalene of 99% purity (1mg/L) was purchased from Aldrich (USA). Silica Gel 60 (72-250 mesh) and aluminum oxide (alumina B super I, 70-290 mesh) chromatography grade were purchased from ICN (Eschwege, Germany). All adsorbent materials were dried at 220°C prior to use. The following solvents of GC- grade were purchased from Riedel-de Haën (Germany) and used as it is: n-hexane, toluene, ethyl acetate, cyclohexane and dichloromethane.

### 2.2 Sampling and Sample Locations

The samples were taken from the eight different locations as shown in Figure 1, at a depth between 30-85 m. From each site three portions, each 3 –5 kg were gathered. All portions were crushed to a fine grain size (Temamael A-11 / Germany) and sieved using ASTM sieves with 1.18 mm pore size. An analytical sample of ca. 100 g was taken and the rest was kept in a cold and dark place to be used later if necessary.

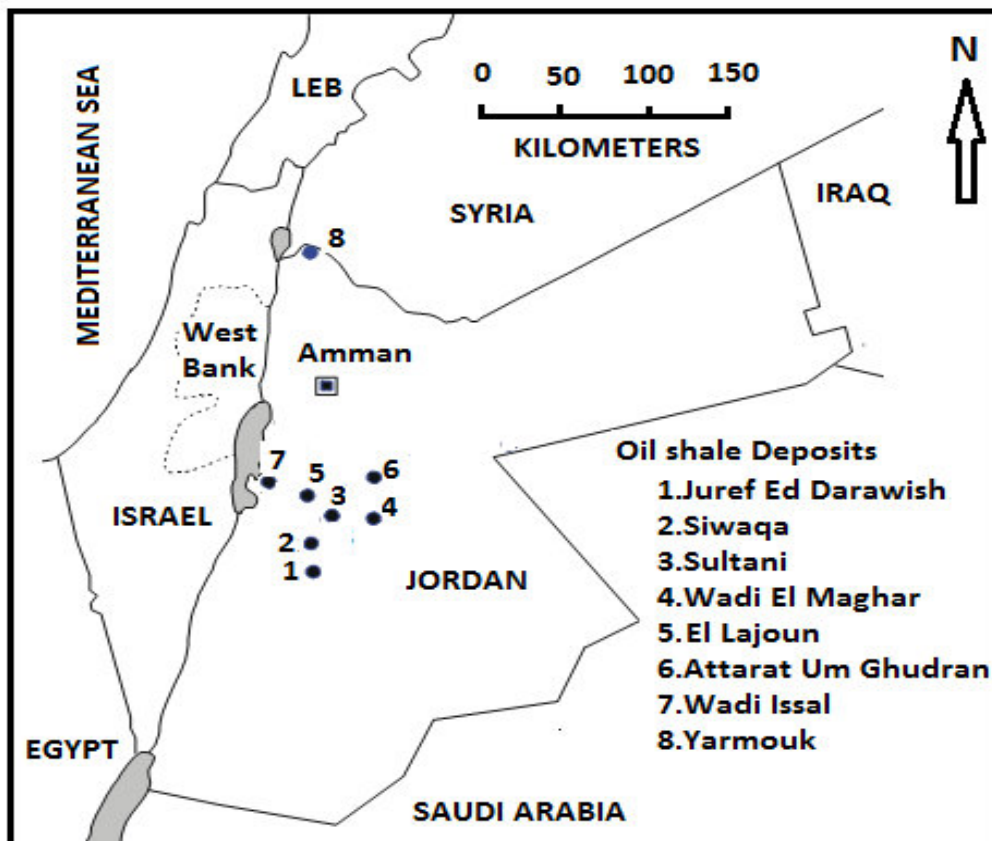


Figure 1: Location map of the oil shale deposits

### 2.3 Gel Permeation Chromatographic Apparatus (GPC)

Gel permeation chromatographic apparatus consisted of 400 mm× 25 mm glass column, two adjustable plungers, O-rings, PTEF tubing and an injector with 3.0 ml sample loop of PTFE tubing was used. The gel permeation chromatographic column was packed with Bio-Beads S-X3; 200-400 mesh (Bio-Rad, California).

The GPC column was tested for fractionation and the percent recovery through the injection of 2.5 ml of a known concentration (1 ppm) of polycyclic aromatic hydrocarbon standard mixture. The GPC column was eluted with cyclohexane: ethyl acetate (1:1). It was found that the fraction 110-320 mL contains all the compounds of the standard polycyclic aromatic hydrocarbons with 92-100% recovery.

### 2.4 Sample Extraction and Clean-Up

Ten grams of each homogenized soil sample were extracted in a soxhlet apparatus, for 16 hours (20 cycles) using 150 ml toluene. The extracts were then evaporated nearly to dryness using the rotary evaporator at 40°C and 78 mbar. The residue was evaporated completely to dryness with a gentle stream of nitrogen and reconstituted in 3 ml cyclohexane: ethyl acetate (1:1). 2.5 ml were injected onto the GPC- column which was eluted at a flow rate of 5 ml/ min with cyclohexane: ethyl acetate (1:1). The first 110 ml were discarded and next 210 ml were collected. The volume of this fraction was reduced through evaporation at 40°C and 276 mbar to ca. 0.5 mL. The column was then washed with ca. 100 mL of the same eluent to be ready for next sample (Alawi *et al.*, 1995). The sample fraction from the GPC column (210 ml) was evaporated at 40°C and 275 mbar to 0.5 ml. The raw extract from the GPC-step was cleaned up according to ( C.P.E.T, 1999) method with a slight modification. A glass column (30 x 1.6 cm) was prepared as follows: 11 g of dry (220°C, 2h) silica gel were filled into the column, one gram of 5% deactivated alumina then 2 g of

anhydrous sodium sulfate were added. This column was washed with 50 ml dichloromethane and 30 ml n-hexane. The residues from the GPC-extraction step (0.5 mL) were added to the silica-alumina column and eluted with 23 ml n-hexane (alkane fraction/ discard). The PAHs were eluted from the column with 25 mL n-hexane: dichloromethane (1:1). The eluate was evaporated at 40°C and 335 mbar to 1ml, then to dryness using a gentle stream of nitrogen. The residues were dissolved in 500 µL n-hexane containing 1 µg/ml internal standard (1-Fluoronaphthalene) then transferred into 500 µL screw cap-vial with a glass inserts and 2 µL were injected onto the GC/MSD- column ( Wenzel *et al.*, 2002).

## 2.5 Chromatographic Conditions and MS-Detection

The GC-MS analysis was carried out using an HP-6890 gas chromatograph, an autosampler series 7683 and an HP-5973 quadrupole mass spectrometer from Agilent Technologies (Waldron/Germany) under the following conditions:

**Injected volume** 2 µL/ splitless, **Column:** DB-5, 30 m, 0.25 mm I.D; 0.25 µm film thickness, and stationary phase: 95% dimethyl – 5% phenyl polysiloxan; **Carrier gas:** Helium (99.999 %), (8 psi); **Temperature program:** 100° C (10 min), 100-160° C (25 °C /min), 160 °C – 265 °C (5°C/min), 265 °C (17 min); **Detector:** mass selective quadrupole – detector, Agilent 5973 N (MSD); **Auxiliary (transfer line):** 300°C, Electron Impact Ionization; **Ionization Energy:** 70 eV; **Calibration substance:** Perflourotributylamine (PFTBA); **Tuning masses:** 69 / 219 / 502

**Aquisition mode:** Selective ion monitoring (SIM) - mode, quantitation masses, see table 1.

**Table 1: PAHs quantitation masses, according to Peters and Harlin (1995).**

PAH	<i>m/z</i>	PAH	<i>m/z</i>
1-Fluoronaphthalene	146	Chrysene	228
Acenaphthylene	152	Benzo(b)fluoranthene	252
Fluorene	166	enzo(k)fluoranthene	252
Phenanthrene	178	Benzo(a)pyrene	252
Anthracene	178	Indeno(1,2,3 cd)pyrene	276
Pyrene	202	Dibenzo(a,h)anthracene	278
Benzo(a)anthracene	228	Benzo(g,h,i)perylene	276

## 3 Method Validations

### 3.1 Linear Range

For the study of the linear range for all studied thirteen PAH compounds, a dilution standard mixture solution series of 1, 15, 25, 50, 100, 500 and 1000 ng/ml were prepared and injected onto the GC/MS. The calibration curves (peaks area ratio versus concentration) for all compounds were drawn. All relations were found to be linear up to 1000 ng/ml and the correlation coefficients were between 0.9816 and 0.9969.

### 3.2 Detection Limits and Limits of Quantitation

The limits of detection (LODs) and limits of quantitation (LOQs) were determined for all studied PAH-compounds. The calculated LODs represent the lowest concentration levels at which the target compounds could be detected with a signal-to-noise ratio of 3 and found to be ranged between 0.007 and 0.070 µg/kg for PAHs. The LOQs were determined as signal-to-noise ratio of 10 and found to be ranged from 0.020 and 0.234 µg/kg for PAHs. LODs, LOQs and the corresponding retention times of the studied compounds are shown in tables 2.

**Table 2: Elution sequence (Peak Number), retention times, LODs and LOQs of the studied PAHs**

Peak No.	Retention time $t_R$ (min)	Standard of PAHs	LOD ( $\mu\text{g}/\text{kg}$ )	LOQ ( $\mu\text{g}/\text{kg}$ )
1	7.75	1-Fluoronaphthalene (I.S)	-	-
2	13.98	Acenaphthylene	0.007	0.024
3	15.91	Fluorene	0.007	0.023
4	19.00	Phenanthrene	0.009	0.030
5	19.16	Anthracene	0.018	0.059
6	24.54	Pyrene	0.007	0.022
7	29.95	Benzo(a)anthracene	0.009	0.029
8	30.12	Chrysene	0.006	0.020
9	34.69	Benzo(b)fluoranthene	0.064	0.212
10	34.81	Benzo(k)fluoranthene	0.070	0.234
11	36.23	Benzo(a)pyrene	0.058	0.193
12	43.94	Indeno(1,2,3 cd)pyrene	0.022	0.075
13	44.45	Dibenzo(a,h)anthracene	0.028	0.095
14	46.06	Benzo(g,h,i)perylene	0.021	0.068

### 3.3 Precision

#### 3.3a Instrument Precision

The precision of the instrument was measured through the injection of the standard mixture solution at three concentrations (1000, 500, 25 ng/mL). Each solution was injected three times. The instrument precision represents as the average relative standard deviation for the 1000 ng/ml concentration was found in the range 0.89 - 2.53%, for the 500 ng/ml in the range 0.61 - 7.13%, and for the 25 ng/ml in the range 2.99 - 8.15%. All relative standard deviations (RSD) for all concentrations were found less than the accepted limit value for trace analysis (RSD <15%) (Gonzales and Herrador, 2007), this shows that the method has a good instrumental precision.

#### 3.3b Method Precision

The precision of the method was assessed through the analysis of spiked PAHs –free sand samples at five concentrations (25, 50, 100, 500 and 1000 ng/g), each concentration was injected three times. The method precision represents as the relative standard deviation for the 25 ng/g concentration was found in the range 2.69 - 4.11%, for the 50 ng/g in the range 2.21 - 5.85%, for the 100 ng/g in the range 0.62 - 4.51 %, for the 500 ng/g in the range 1.71 - 7.00%, and for the 1000 ng/g in the range 0.95 - 7.06%. All relative standard deviations (RSD) for all concentrations were found to be less than the accepted limit value for trace analysis (RSD <15%) (Gonzales and Herrador, 2007), which means that the method shows a good precision.

### 3.4 Recovery and Accuracy

Five samples, each of ten grams of pure blank sample were spiked with the PAHs standard mixture to give the concentrations of 25, 50, 100, 500 and 1000 ng/g. These samples were mixed thoroughly, extracted and cleaned-up then analyzed according to the above mentioned method. These recovery tests were done in triplicate at different times. The average recoveries were calculated for each concentration by dividing the found (measured) value by the true value, then multiplying with 100%. The recovery results are shown in Table 3. These results show that there is an increase in the recoveries by increasing the spiked concentration.

All recoveries were found lie within the acceptable range for trace analysis of 80-120 % (Gonzales and Herrador, 2007).

From these recovery results, the difference between the true values and the measured values give a good idea about the accuracy, where it was calculated as “Relative Absolute Error”. The results are shown in Table 4.

**Table 3: Results of recovery study**

Spiked concentration → PAHs ↓	25 ng/g	50 ng/g	100 ng/g	500 ng/g	1000ng/g
	$\bar{X} \pm S$ (n = 3)	$\bar{X} \pm S$ (n = 3)	$\bar{X} \pm S$ (n = 3)	$\bar{X} \pm S$ (n = 3)	$\bar{X} \pm S$ (n = 3)
Acenaphthylene	72.34 ± 2.97	78.86 ± 2.20	82.86 ± 1.98	85.64 ± 3.19	81.69 ± 1.49
Fluorene	88.10 ± 3.03	90.02 ± 2.41	91.62 ± 4.45	86.66 ± 1.85	92.39 ± 3.14
Phenanthrene	93.30 ± 3.37	91.53 ± 3.08	82.61 ± 2.87	106.29 ± 2.72	90.64 ± 1.96
Anthracene	91.54 ± 2.58	84.40 ± 4.94	78.43 ± 2.34	93.11 ± 6.52	85.15 ± 4.64
Pyrene	99.30 ± 2.77	96.64 ± 2.31	92.06 ± 2.45	101.00 ± 1.72	91.26 ± 1.10
Benzo(a)anthracene	93.64 ± 3.52	92.83 ± 4.31	96.03 ± 4.33	92.04 ± 2.06	89.98 ± 1.63
Chrysene	99.85 ± 2.69	91.59 ± 4.93	100.17 ± 1.64	97.07 ± 2.17	97.93 ± 2.42
Benzo(b)fluoranthene	101.80 ± 2.81	103.97 ± 5.04	100.88 ± 0.63	95.03 ± 2.58	100.48 ± 0.95
Benzo(k)fluoranthene	90.97 ± 3.37	90.75 ± 2.10	93.20 ± 3.02	92.68 ± 2.47	95.00 ± 3.21
Benzo(a)pyrene	90.89 ± 3.52	91.32 ± 4.50	90.22 ± 3.13	98.37 ± 2.14	100.60 ± 2.59
Indeno(1,2,3cd)pyrene	84.10 ± 4.27	91.10 ± 2.56	95.87 ± 3.09	94.38 ± 3.00	99.56 ± 7.03
Dibenzo(a,h)anthracene	95.61 ± 2.57	94.75 ± 3.68	91.96 ± 3.58	98.12 ± 2.69	102.79 ± 3.01
Benzo(g,h,i)perylene	96.05 ± 3.45	91.55 ± 3.74	97.55 ± 2.14	92.29 ± 2.03	98.66 ± 6.28

**Table 4: Accuracy calculated as the relative absolute error at different concentrations of PAHs in spiked blank sand**

Standard of PAHs	Relative Absolute Error at 25 ng/g	Relative Absolute Error at 50 ng/g	Relative Absolute Error at 100 ng/g	Relative Absolute Error at 500 ng/g	Relative Absolute Error at 1000 ng/g
Acenaphthylene	27.66	19.14	21.14	8.45	11.31
Fluorene	9.24	9.98	9.98	13.34	7.61
Phenanthrene	5.37	8.47	8.47	6.29	4.36
Anthracene	10.79	15.60	15.60	6.89	4.85
Pyrene	2.97	4.64	3.36	1.00	1.74
Benzo(a)anthracene	9.36	13.83	7.17	7.96	5.02
Chrysene	6.85	6.59	8.41	2.93	2.07
Benzo(b)fluoranthene	6.13	1.97	3.97	4.97	0.48
Benzo(k)fluoranthene	9.03	5.75	9.25	4.97	5.00
Benzo(a)pyrene	13.78	8.68	8.68	1.63	0.60
Indeno(1,2,3 cd)pyrene	15.90	8.90	8.90	5.62	0.44
Dibenzo(a,h)anthracene	2.39	5.25	5.25	1.88	2.79
Benzo(g,h,i)perylene	2.05	8.45	8.45	7.71	1.34

## 4. Results and Discussion

### 4.1 Content of the Real Samples

The oil shale samples were analyzed according to the above mentioned and validated method. Each sample was analyzed three times (weighing, soxhlet extraction, GPC-clean up and silica-column clean up) and each extract was injected onto GC/MS-column three times. Table 5 shows the recovery corrected average concentrations of the studied PAHs in oil shale samples. Table 6 shows the toxicity equivalent concentrations for all compounds in all samples in the ng TEQ/g unit, calculated from the average concentrations in Table 5 and the toxicity equivalency factors (TEF) shown in table 6, using the B(a)P toxic equivalency factors (TEF) recommended for use by the US EPA (USEPA, 1993). Comparing the concentration of the studied thirteen compounds in all samples and as shown in Figure 2, one notice that acenaphthylene was found in the concentration range between 5.56 µg/kg (Attarat Um Ghudran) and 86.64 µg/kg (Sultani), fluorene between 6.80 µg/kg (Jurf Ed Drawish) and 348.38 µg/kg (Yarmouk), phenanthrene between 8.87 µg/kg (Wadi El Magar) and 943.63 µg/kg (Wadi Issal), anthracene between 2.10 µg/kg (Wadi El Magar) and 49.88 µg/kg (Yarmouk), pyrene between 12.58 µg/kg (Wadi El Magar) and 165.24 µg/kg (Wadi Issal), benzo(a)anthracene between 3.34 µg/kg (Jurf Ed Darawish) and 131.54 µg/kg (Siwaqa), chrysene between 4.66 µg/kg (Jurf Ed Drawish) and 457.24 µg/kg (Siwaqa), benzo(b)fluoranthene between 1.11 µg/kg (Attarat Um Ghudran) and 73.66 µg/kg (Siwaqa), benzo(k)fluoranthene between 0.71 µg/kg (Attarat Um Ghudran) and 61.50 µg/kg (Wadi Issal), benzo(a)pyrene between 3.60 µg/kg (Jurf Ed Drawish) and 217.11 µg/kg (Wadi Issal), indeno(1,2,3-cd) pyrene between 6.71 µg/kg (Attarat Um Ghudran) and 40.18 µg/kg (Siwaqa), dibenzo(a,h)anthracene between 0.77 µg/kg (Attarat Um Ghudran) and 87.94 µg/kg (Siwaqa), benzo(g,h,i)perylene between 7.39 µg/kg (Jurf Ed Drawish) and 138.66 µg/kg (Sewaqa). Figure 2 shows also these results in a histogram form.

**Table 5: Recovery corrected average concentrations of the studied samples in ng/g (n = 3)**

Sample sites → Comp'd ↓	Yar- mouk	Attarat Um Ghudr-an	El Lajjun	Wadi El Maghar	Juref Ed Dara- wish	Sultani	Wadi Issal	Siwaqa
Acenaphthylene	23.22 ±2.86	5.56 ±1.71	72.98 ±2.24	20.00 ±4.16	9.50 ±1.91	86.64 ±4.87	11.79 ±0.56	8.50 ±1.10
Fluorene	45.20 ±3.32	10.82 ±0.32	51.80 ±1.69	7.09 ±2.73	6.80 ±1.04	40.40 ±3.96	201.69 ±3.92	18.96 ±3.12
Phenan- threne	348.3 8±11. 75	25.18 ±0.36	139.15 ±4.90	10.69 ±2.94	31.95 ±2.37	138.57 ±4.32	1036.9 6 ±5.12	35.24 ±2.93
Anthra- cene	58.68 ±0.86	22.92 ±1.96	20.06 ±1.13	2.36 ±0.82	8.53 ±1.73	24.34 ±2.27	38.43 ±2.58	20.34 ±1.99
Pyrene	76.28 ±4.29	63.33 ±0.96	23.26 ±2.03	12.58 ±3.11	12.87 ±1.61	68.61 ±0.93	181.58 ±3.56	79.04 ±4.31
Benzo(a) anthracene	25.98 ±1.25	44.68 ±1.18	45.44 ±3.58	21.47 ±4.80	2.93 ±0.60	90.99 ±1.08	61.49 ±3.44	146.16 ±0.50
Chrysene	78.80 ±3.21	28.00 ±1.41	29.08 ±2.63	14.66 ±3.42	4.36 ±1.14	72.18 ±2.71	295.67 ±2.43	466.57 ±4.76

Benzo(b)-fluoranthene	1.72 ±0.55	1.17 ±0.45	ND	14.66 ±1.48	3.40 ±0.55	ND	ND	73.66 ±0.33
Benzo(k)-fluoranthene	5.85 ±1.68	0.78 ±0.74	3.13 ±1.17	3.17 ±0.88	ND	21.52 ±2.82	64.74 ±0.58	49.87 ±0.28
Benzo(a)-pyrene	29.92 ±2.29	6.79 ±1.57	8.90 ±.80	13.19 ±2.11	3.91 ±1.04	14.853 ±3.08	214.96 ±4.22	47.77 ±2.08
Indeno(1,2,3 cd)pyrene	ND	7.98 ±3.02	ND	ND	ND	20.29 ±2.44	ND	42.74 ±0.33
Dibenzo(a,h)-anthracene	ND	0.80 ±0.47	ND	ND	ND	19.08 ±2.62	ND	85.38 ±2.83
Benzo(g,h,i)-perylene	19.13 ±0.99	33.25 ±1.74	44.02 ±2.24	23.67 ±5.34	8.21 ±1.59	51.32 ±1.63	70.71 ±1.97	140.06 ±2.39
Total (µg/kg)	713.15 ±33.05	251.26 ±15.91	437.83 ±22.41	134.08 ±31.79	92.46 ±13.58	648.80 ±32.67	2178.03 ±28.38	1214.29 ±24.95

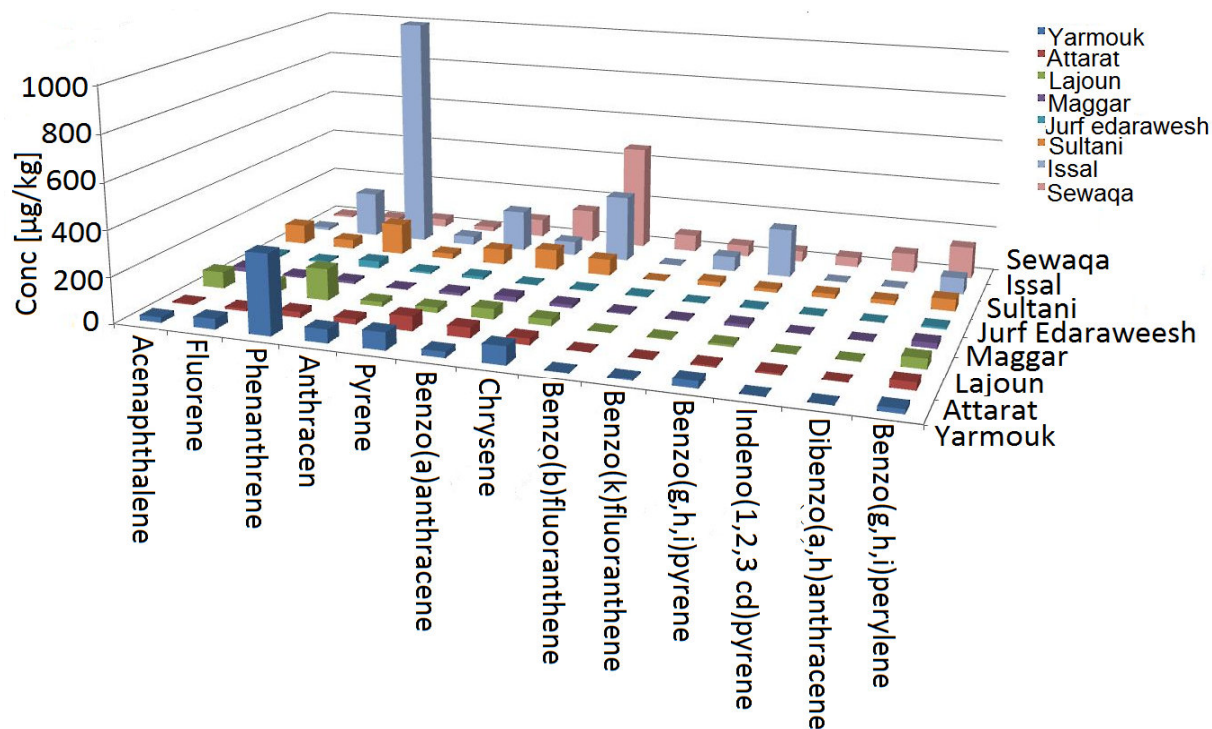


Figure 2: Total Concentrations of PAHs in oil shale from the major deposit sites



The highest total concentration of all studied PAHs was found in Wadi Issal (2178.03  $\mu\text{g}/\text{kg}$ ) followed by Siwaqa (1214.29  $\mu\text{g}/\text{kg}$ ). The same trend was found for the toxicity equivalent concentrations (Table 6) where the highest value was found in Wadi Issal sample (233.06 ng TEQ/g) followed by Siwaqa sample (170.80 ng TEQ/g).

Comparing the total concentrations of the studied PAHs in the Jordanian oil shale samples with other types of samples like soil, we found that our samples contain less concentrations (range: 92- 2178ng/g) compared to those found in soil samples from Beijing/ China (range 93 – 13141 ng/g) (Peng *et al.*, 2011), and less than those found in soil samples from Agra/ India (range: 3100 - 28500 ng/g) (Masiha and Taneja, 2006) and less than those found in soil samples from Ruseifa/ Jordan (range: 286,000 - 1704,000 ng/g ) (Jiries *et al.*, 2005).

Upon comparing the total concentrations of the studied PAHs in the Jordanian oil shale samples with other types of fuel, we found that our samples contain less concentrations compared to those found in Hard-coal briquette samples (27420 ng/g) and those found in Brown-coal briquette (36540 ng/g) (Grimmer *et al.*, 1983).

**Table 6: Toxicity equivalent (TEQ) concentrations for all studied samples**

Comp'd	* TEF	Corrected concentrations in [ng TEQ / g]							
		Yar-mouk	Attarat Um Ghudran	El Laj-jun	Wadi El Maghar	Juref Ed Dara-wish	Sultani	Wadi Issal	Siwaqa
Acenaphthylene	0.001	0.02	0.01	0.07	0.02	0.01	0.09	0.01	0.01
Fluorene	0.001	0.05	0.01	0.05	0.01	0.01	0.04	0.20	0.02
Phenanthrene	0.001	0.35	0.03	0.14	0.01	0.03	0.14	1.04	0.04
Anthracene	0.010	0.590	0.23	0.20	0.02	0.09	0.24	0.38	0.20
Pyrene	0.001	0.08	0.06	0.02	0.01	0.01	0.07	0.18	0.08
Benzo(a)anthracene	0.100	2.06	4.47	4.54	2.15	0.29	9.10	6.15	14.62
Chrysene	0.010	0.79	0.28	0.29	0.15	0.04	0.72	2.96	4.67
Benzo(b)-fluoranthene	0.100	0.17	0.12	0.00	0.52	0.34	0.00	0.00	7.37
Benzo(k)-fluoranthene	0.100	0.58	0.08	0.31	0.321	0.00	2.15	6.47	4.99
Benzo(a)-pyrene	1.000	29.92	6.79	8.90	13.19	3.91	14.85	214.96	47.77
Indeno(1,2,3cd)pyrene	0.100	0.00	0.80	0.00	0.00	0.00	2.03	0.00	4.27

Dibenzo(a,h)-anthracene	1.000	0.00	0.80	0.00	0.00	0.00	19.08	0.00	85.38
Benzo(g,h,i)-perylene	0.010	0.19	0.33	0.44	0.24	0.08	0.51	0.71	1.40
Total (ng TEQ/g)	-	35.34	14.00	14.98	16.63	4.81	49.02	233.06	170.80

\* TEF = Toxicity equivalency factor according to Grimmer *et al.* (1983)

### 3.2. Cancer Risk Assessment

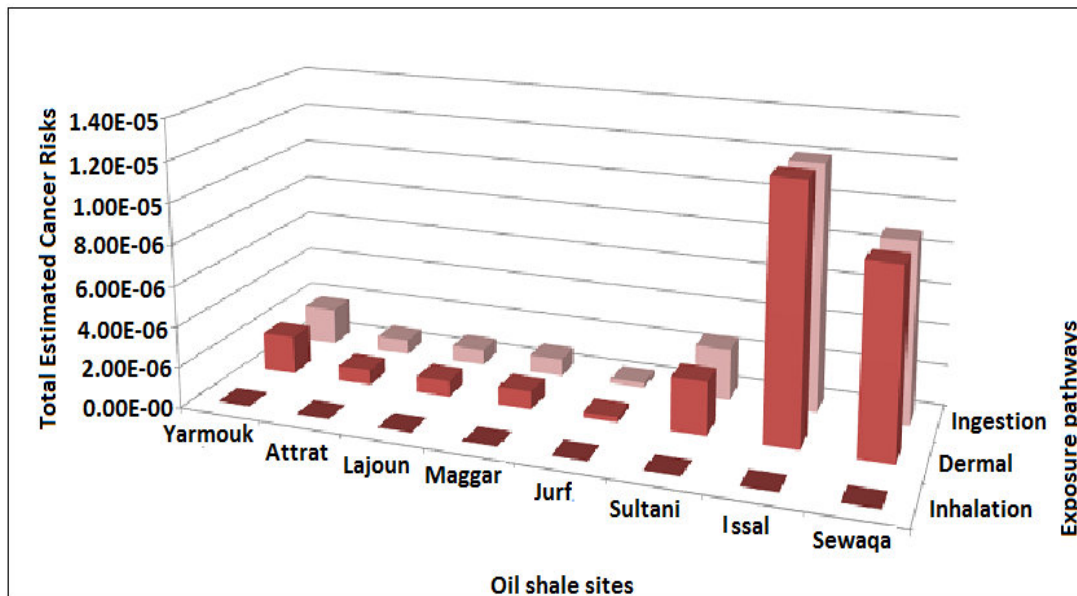
The values of total estimated cancer risk of the samples shown in Table 7 and used to draw figure 3 were calculated using the Incremental Life Cancer Risk (ILCR) equation given in (Canadian Council, 2008). Table 7 shows the total calculated incremental lifetime cancer risks (ILCRs) from exposure to PAHs in Jordanian oil shale by ingestion, dermal and inhalation exposure pathways, to an individual exposed for 70 years, starting at birth using the (USEPA 1991 and 2004) recommended standard default exposure parameters for a Reasonable Maximum Exposure (RME) resident.

**Table 7: Total incremental lifetime cancer risks (ILCR) from exposure to PAHs in Jordanian oil shale through all exposure pathways**

Oil shale sites → Exposure Pathway	Yarmouk	AttaratUm Gudran	El Lajjun	Wadi El Maghar	Juref Ed Darawish	Sultani	Wadi Issal	Siwaqa
	<b>Direct Ingestion</b>	$1.89 \times 10^{-6}$	$7.47 \times 10^{-7}$	$7.99 \times 10^{-7}$	$8.87 \times 10^{-7}$	$2.57 \times 10^{-7}$	$2.62 \times 10^{-6}$	$1.24 \times 10^{-5}$
<b>Dermal Contact</b>	$1.96 \times 10^{-6}$	$7.87 \times 10^{-7}$	$8.32 \times 10^{-7}$	$9.24 \times 10^{-7}$	$2.67 \times 10^{-7}$	$2.72 \times 10^{-6}$	$1.29 \times 10^{-5}$	$9.49 \times 10^{-6}$
<b>Inhalation</b>	$3.93 \times 10^{-11}$	$1.55 \times 10^{-11}$	$1.67 \times 10^{-11}$	$1.85 \times 10^{-11}$	$5.35 \times 10^{-12}$	$5.45 \times 10^{-11}$	$2.59 \times 10^{-10}$	$1.89 \times 10^{-10}$
<b>Total ILCR*</b>	$3.85 \times 10^{-6}$	$1.53 \times 10^{-6}$	$.63 \times 10^{-6}$	$1.81 \times 10^{-6}$	$5.25 \times 10^{-7}$	$5.34 \times 10^{-6}$	$2.54 \times 10^{-5}$	$1.76 \times 10^{-5}$

The highest total estimated cancer risks were found in Wadi Issal and siwaqa region. In comparison, the total estimated cancer risks in Jurf Ed Drawish were significantly lower, as shown in Figure 3. According to the above mentioned USEPA guideline in regulatory terms, an estimated cancer risks of  $10^{-6}$  or less denotes virtual safety and an estimated cancer risks of greater than  $10^{-4}$  denotes potentially high risk (Liao and Chiang, 2006; USEPA, 1989).

The estimated cancer risks under normal exposures to Jordanian oil shale-PAHs for all age groups in most of locations are equal or less than  $10^{-6}$ . Under worst-case scenario, no estimated cancer risks of the extreme exposures exceeded  $10^{-4}$ .



**Figure 3: The total estimated cancer risks of exposure to Jordanian oil shale-PAH through different exposure pathways**

By multiplying the estimated cancer risks of exposing to Jordanian oil shale-PAHs by  $10^6$ , it is possible to determine the theoretical number of cancer cases per million of people. For example ( $2.54 \times 10^{-5}$ ), this means that the number of people who are suspected of cancer due to exposure to oil shale-PAHs in the area of Wadi Issal is two out of every hundred thousand or twenty-five of every million.

In other meaning if a person was exposed to the highest level of BaP - TEQ in the Wadi Issal oil shale for 70 years, he has 25 in million increased chance of cancer from this exposure, this is the highest estimate of the risk and the actual risk is likely lower.

#### 4. Conclusions

A comprehensive study was performed to monitor the concentrations of PAHs in Jordanian oil shale samples from eight deposits. It was possible to determine the concentrations of thirteen PAHs in the studied samples.

The studied PAH compounds were found in almost all samples. The total concentration of the studied PAHs were ranged from (92.49 ng/g) in Jurf Ed Drawish to (2178.03 ng/g) in Wadi Issal.

The total estimated cancer risks associated with the exposure to Jordanian oil shale-PAH for all age groups and in all sites were found to be acceptable. Even under the worst-case scenario, the estimated cancer risk for adults and children in all sites are lower than the acceptable range of excess cancer risk of  $1.0 \times 10^{-4}$  –  $1.0 \times 10^{-6}$ , specified by the US Environmental Protection Agency.

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