

**RESIDUE ANALYSIS OF ORGANIC POLLUTANTS  
IN SEDIMENTS FROM THE AMMAN/ZARQA AREA  
IN JORDAN. PART I: DEVELOPMENT OF ANALYTICAL  
METHODS AND DISTRIBUTION PATTERNS OF PAHS**

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# RESIDUE ANALYSIS OF ORGANIC POLLUTANTS IN SEDIMENTS FROM THE AMMAN/ZARQA AREA IN JORDAN. PART I: DEVELOPMENT OF ANALYTICAL METHODS AND DISTRIBUTION PATTERNS OF PAHS

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## SUMMARY

The present work was aimed at investigating the concentration levels and seasonal distribution patterns of US-EPA PAH of Zarqa River sediments in Jordan. Sediment samples were collected along Zarqa River and its main two tributaries in the periods of December 2000 and from November 2001 until January 2002. Sophisticated extraction and clean-up procedures were developed and optimized. PAH concentrations were determined using GC/MS in SIM mode. The results have shown that the total concentrations of PAH during the summer season (dry period) were 2-3 times higher than during the winter season (wet period) and they significantly correlated with TOC. Near the sources of Zarqa River as well as in the winter sampling period the sediment profiles were characterized by 2-3 ring PAHs, while 4-6 ring PAHs dominated downstream and during the summer sampling period. The present work is a first report. It evaluates the environmental quality and measures the background concentrations of PAHs in the Amman/Zarqa area in Jordan.

## KEYWORDS:

PAH, sediments, TOC, Zarqa River, Jordan.

## INTRODUCTION

The United States Environmental Protection Agency (US-EPA) has defined 16 polycyclic aromatic hydrocarbons (PAH) as priority pollutants. Their behavior and distribution in different environmental compartments have been the hot subject of continued research [1-5].

PAHs are formed and released into the environment through natural and anthropogenic sources. The natural sources include volcanic activities and forest fires, whereas anthropogenic sources mainly originate from incomplete combustion processes of liquid fuel and coal, incineration, domestic and industrial waste disposals [6]. PAHs tend to accumulate in sediments and are found to be linearly correlated with the total organic carbon (TOC) [7, 8].

PAHs enter and pollute the Zarqa River ecosystem and mainly originate from surface runoff, municipal and industrial activities. Their rate increased, especially after commissioning the largest wastewater stabilization pond (As-Samra WSP) in Jordan in 1985, which serves more than 52% of the kingdom's population. In addition, more than 80% of the national industries are located in the investigated area. A number of studies of inorganic contaminants along Zarqa River were carried out and all indicated detrimental effects on the environmental quality [9-11]. However, the organic contamination fate for Zarqa River is not known yet.

The objectives of this work were focused on developing and optimizing an analytical procedure to investigate a wide range of organic pollutants in river sediments which heavily contaminated domestic and industrial wastewater effluents. Furthermore a field monitoring study should be carried out to evaluate the environmental quality and to measure PAH background concentrations in Zarqa River ecosystem.

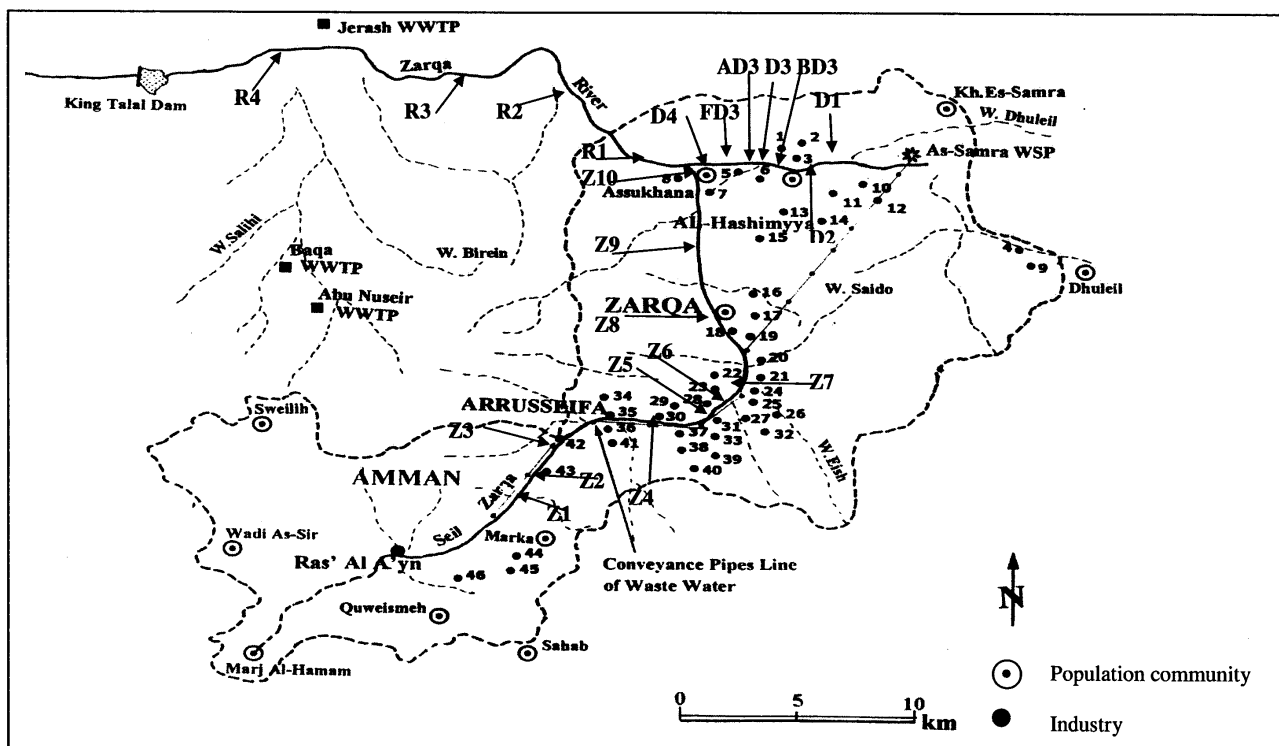


FIGURE 1  
The study area with the distribution of industries and sampling sites.

## MATERIALS AND METHODS

### Study area and sampling strategy

Jordan is dominated by Mediterranean climate. The average rainfall ranges from 600 mm/yr in the north to less than 50 mm/yr in the south and east. The study area is located at the northeast part of the country, which is presented by Zarqa River basin and spreads over 3,900 km<sup>2</sup>. The source of Zarqa River is Amman city at Ras' Al Ayn spring, where it starts as Seil Zarqa and flows northeast of Amman City. Then, it passes Zarqa City and leaves the urban area to join Wadi Dhuleil near Assukhana area, and subsequently, it turns west to flow via King Talal Reservoir (KTR). Downstream of KTR, it joins Jordan River and their waters are used for irrigation purposes. Zarqa River is the second largest river in Jordan, and its average annual discharge was 65 million m<sup>3</sup>/yr until 1976, after that the annual discharge has been changed due to construction of KTR in 1977 and establishment of As-Samra WSP in 1985 [12]. The study area with the distribution of industries and sampling sites is presented in Figure 1.

The investigated area is divided into three categories. The first one is Seil Zarqa tributary (Z) which passes Amman and Zarqa Cities. During summer season the water flow is limited and the drainage system of Seil Zarqa is mainly supplied by industrial effluents, dis-

charges of agricultural irrigation, and effluents of municipal wastewater as well as leakages of untreated wastewater from the sewerage. The second category is Wadi Dhuleil (D) where the drainage system is mainly affected by As-Samra WSP and some industrial wastewater effluents. Finally, category R represents Zarqa River itself after the confluence of both tributaries (Z and D).

Sediment samples were taken from all these sites at different distances. In addition, non-polluted reference samples were taken 120 km south of Amman City.

The sampling activities were carried out in November 2001 and January 2002, defined as summer (dry) and winter (wet) seasons, respectively. Surface sediment samples (0-5 cm) were collected from one square meter at each bank of the drainage system, pooled and homogenized to get representatively mixed samples. They were stored in glass jars until they were transported to the laboratory of Mu'tah University. Then the samples were wet sieved for < 2 mm, centrifuged and stored at -20 °C until analysis. Crude stable sediment extracts were prepared in the Soil Department at Mu'tah University, Al-Karak, Jordan, and were then transported to Braunschweig, Germany, under cold condition. Clean-up procedure and analysis were performed at the Institute of Ecological Chemistry and Waste Analysis of the Technical University of Braunschweig.

### Sample preparation and analysis

Homogenized sediment samples containing 30 g of dry material were used for extraction. They were ground and mixed well with 70 g sea sand and 70 g anhydrous sodium sulfate using a 500 g porcelain mortar. The homogenized mixture was transferred into the extraction column (35 cm length, 5.7 cm inner diameter), which was rinsed 2 times with acetone and one time with n-hexane prior to use. Then it was plugged with a piece of glass wool and 5 g of anhydrous sodium sulfate. The target compounds were extracted overnight with 450 mL of n-hexane and acetone mixture (2:1), the flow rate was adjusted to 1 mL/min. The crude extract was rotary-evaporated and concentrated nearly to dryness in a gentle nitrogen stream and dissolved in 5 mL of ethyl acetate and cyclohexane mixture (1:1). The extract was filtered through a 0.47  $\mu\text{m}$  PTFE syringe filter directly before GPC injection which was purchased from Macherey-Nagel, Germany. The GPC column was packed with Bio-beads S-X8 (200-400 mesh) (Bio-Rad, USA). The fraction was collected in the interval of 110-380 mL containing the analytes. The solution was rotary-evaporated and concentrated nearly to dryness using nitrogen stream and dissolved in 1 mL n-hexane, appearance of precipitate at this step was observed for most of the samples. The solution was quantitatively transferred into the neutral alumina column (10 g of partly deactivated neutral alumina (12.5%, 70-230 mesh, Merck, Germany), and 1 g of dried anhydrous  $\text{Na}_2\text{SO}_4$  on the top of the chromatographic column). The non-polar fraction was eluted with 60 mL n-hexane and rotary-evaporated to 1 mL. In order to eliminate most of interfering substances for the final GC analysis, a further clean-up procedure was performed to separate target compounds into two fractions. The chromatographic column was packed with 10 g of fully activated silica gel (70-230 mesh, Merck, Germany), and 1 g of oven-dried anhydrous  $\text{Na}_2\text{SO}_4$  on the top. This column was eluted into two fractions: The first fraction was eluted with 65 mL n-hexane, which was further analyzed for organochlorine compounds. The second fraction was eluted with 50 mL of ethyl acetate and n-hexane mixture (1:1) and analyzed for PAHs and organochlorine pesticides. All solvents used were of residue grade (Merck, Germany). Before the chromatographic analysis, the elemental sulfur was removed from both silica gel fractions using tetra butyl ammonium sulfite method [13]. The occurrence of the organochlorine compounds in sediment is published in Part II of this project [14].

Total organic carbon (TOC) was determined according to Walkley-Black's wet oxidation method and the results were confirmed using infrared analyzer method [14]. The sediment texture was determined using hydrometer method [14]. GC/MS determination was performed using a Hewlett-Packard HP 5890 Series II gas chromatograph, equipped with HP 7673 KAS 2 programmable auto injector and operated at 80 °C to 350 °C at 13.5 °C/s. The gas chromatograph was coupled to an

HP 5970 Series mass selective detector (MSD) with electron impact ionization mode (EI) and the ionization source was supplied at a voltage of 70 eV. The mass spectrometer was operated in selected ion monitoring mode (SIM) detecting the  $\text{M}^+$  ions for 16 PAH. A 30 m DB-5 MS fused silica capillary column was used with 0.25  $\mu\text{m}$  film thickness and 0.25 mm inner diameter (J&W Scientific, USA). The oven temperature program was started at 60 °C (4 min), ramped at 15 °C/min to 160 °C, then at 3 °C/min to 280 °C (10 min). The transfer line temperature was maintained at 280 °C, the carrier gas (He) flow rate was 1 mL/min and the injection volume 1  $\mu\text{L}$ . External standardization was performed for 16 PAH quantification using matrix standards ranged from 100 to 3000  $\text{pg}/\mu\text{L}$ , which were prepared from US-EPA 16 PAH standard solution of 100  $\text{ng}/\mu\text{L}$  (Promochem, Germany). The correlation coefficients for the calibration curves exceeded 0.998.

## RESULTS AND DISCUSSION

The results of TOC determined by the wet oxidation method and infrared gas analyzer method yielded consistent results. The analytical repeatability of the PAH results expressed as a relative standard deviation (RSD) were generally acceptable, mostly less than 10% for both sampling periods. Naphthalene made an exception in the summer sampling period. It has shown a high RSD (34.6%) value due to its high volatility. The analytical method has shown good recoveries for PAHs which ranged from 62 to 98%. However, the lowest recovery rate of 62% was obtained for naphthalene and the rest recoveries were 70-98%. The sediment texture among all collected samples was characterized by sandy clay loam to loamy sand. The pH values for both sampling periods ranged over 6.2-8.2. More than 80% of the analyzed samples were found within a pH range over 7.0-8.0. That might reflect the composition of the parent materials for dust, soil, and sediments which are dominated by a high carbonate ( $\text{CaCO}_3$ ) content (20-25%) [15, 16].

### Distribution of TOC and PAH

The TOC ranged over 1.43-28.1%  $\pm$  8.13% with an average of 10.3% for summer, and over 0.70-34.7%  $\pm$  7.48% with an average of 6.08% for winter. The variability of organic matter content was dependent on the type of anthropogenic activity at the site, amount of waste effluent as well as on the rainfall quantities. The distribution pattern of TOC in both seasons is presented in Figure 2. Wadi Dhuleil contained total organic carbon 2-6 times higher than other categories. That might be explained as a result of the direct discharge of the As-Samra WSP effluents. The maximum TOC was found at sites D2 (28.1%) and WD3 (34.7%) for summer and winter seasons, respectively. Generally, significant correlation was obtained between TOC and  $\Sigma\text{PAH}$ . The correlation coefficients were 0.82 and 0.84 for WZ and WR categories for winter season, except category WD because of its high organic

matter variability. In addition, for summer sampling period the correlation coefficients were 0.95, 0.63 and 0.95 for categories Z, D and R, respectively.

The distribution pattern of total PAH concentrations (sum of 16 priority pollutants:  $\Sigma$ PAH) for both sampling periods are presented in Figure 3. Generally,  $\Sigma$ PAH concentrations during the summer season were found 2-3 times higher than during the winter season. This might be

explained as dilution effect which has been taken place during the wet season after several wash-out events. The presence of “non-contaminated” reference site provided the opportunity to quantify the anthropogenic contamination of the sediments studied, where all sampling sites illustrated higher  $\Sigma$ PAH concentration levels than the reference site (28  $\mu\text{g}/\text{kg}$  d.w.) located far away from heavy anthropogenic activities.

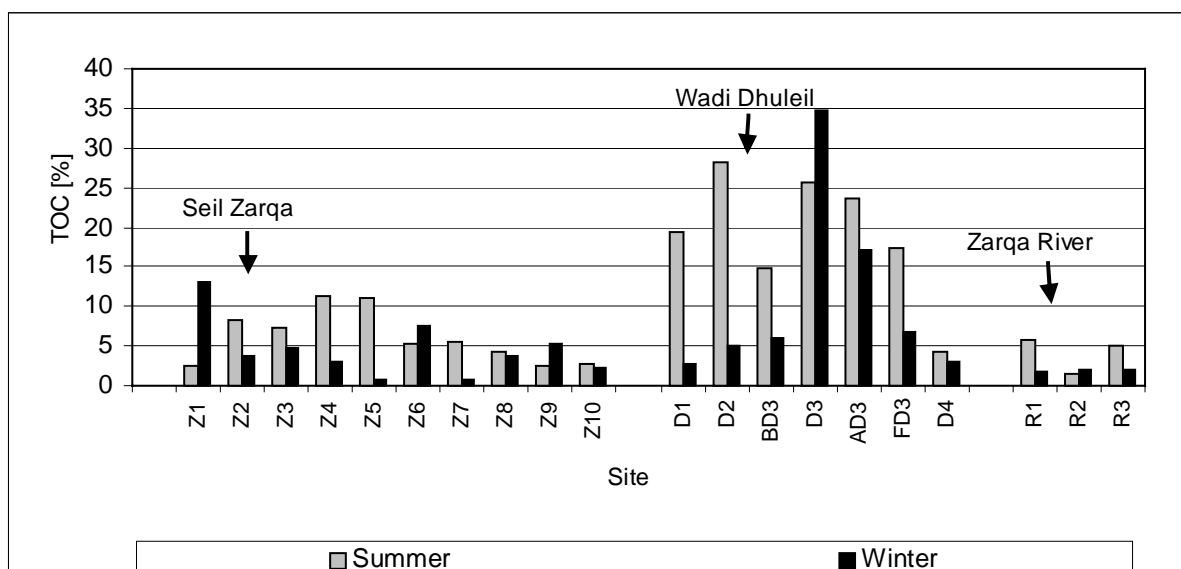


FIGURE 2  
Total organic content (TOC) in summer and winter sampling periods.

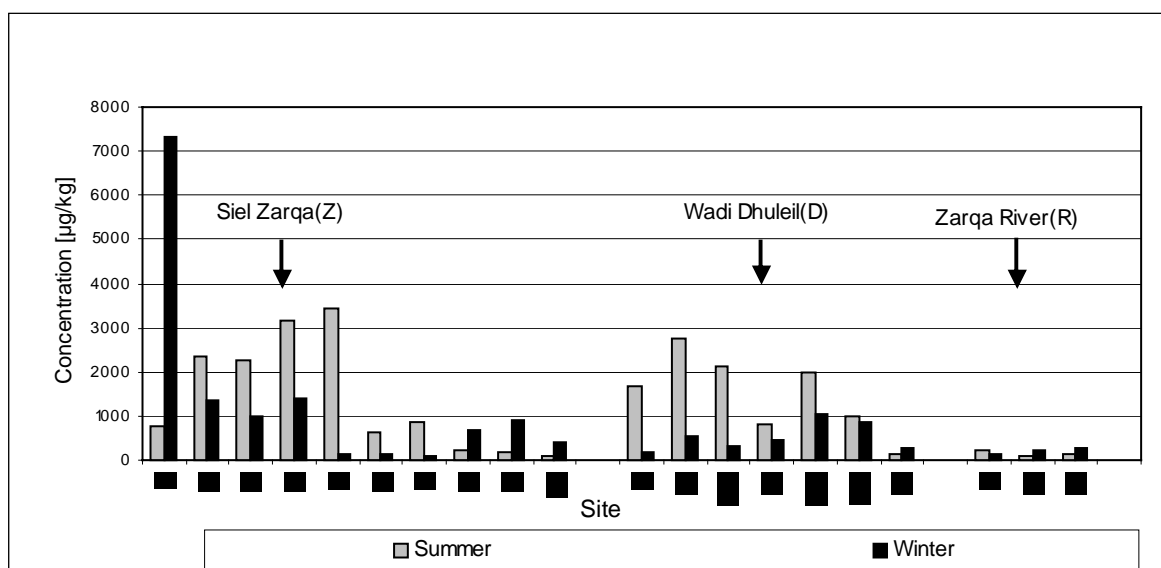
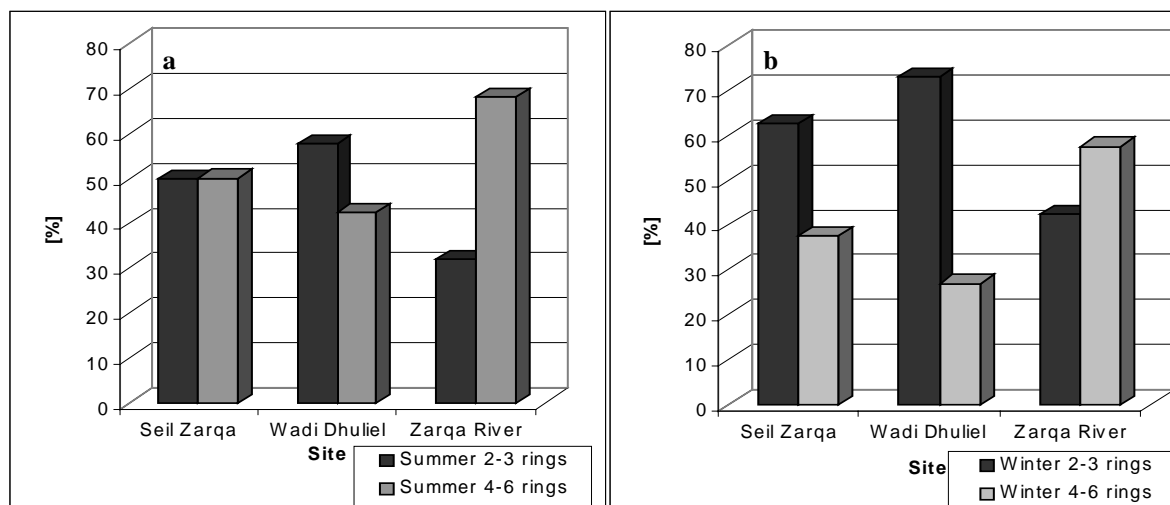


FIGURE 3 - Distribution pattern of  $\Sigma$ PAH in summer and winter seasons, Seil Zarqa (Z1-Z10), Wadi Dhuleil (D1-D4), and Zarqa River (R1-R3).



**FIGURE 4**  
a - PAH profiles in summer ; b - PAH profiles in winter.

#### Summer season

Firstly, for category Z, the total concentrations of PAH increased at sites Z1 to Z5 until reaching a maximum (3,414  $\mu\text{g}/\text{kg}$  d.w.). These sites were affected by heavy industrial activities and high traffic roads at Arrusseifa area. The minimum concentration was found downstream of Seil Zarqa tributary at site Z10 (93  $\mu\text{g}/\text{kg}$  d.w.). Therefore, a limited transport of the sediments along Seil Zarqa is assumed due to limited water flow during dry season leading to an accumulation of the PAHs. Secondly, category D appeared having a particularly high concentration of PAHs because of its high content of organic matter. The maximum  $\Sigma\text{PAH}$  concentration was found at site D2 (2,772  $\mu\text{g}/\text{kg}$  d.w.) and the minimum at site D4 (150  $\mu\text{g}/\text{kg}$  d.w.) downstream of Wadi Dhuleil. Finally, category R has indicated relatively low  $\Sigma\text{PAH}$  concentrations ranging over 69-234  $\mu\text{g}/\text{kg}$  d.w. and remained at the same level along the sampling sites.

#### Winter season

The concentration of the 16 PAHs ranged from 111 to 1,419  $\mu\text{g}/\text{kg}$  d.w. However, the highest concentration (7,319  $\mu\text{g}/\text{kg}$  d.w.) was found at site WZ1, which is located about 6 km behind the source of the Zarqa River. It is the first site along Seil Zarqa which receives wash out waters from the whole Amman catchments area. The sediments at this site are characterized by high TOC (13%), sandy clay loam texture, and are of dark black color. Therefore, wash-out waters were expected to settle their suspended and washed-out materials at this site. Because of its extreme PAH content it was excluded from calculations. The lowest concentration (111  $\mu\text{g}/\text{kg}$  d.w.) was detected at site WZ7, which also contained the lowest TOC value. At Seil Zarqa, the total PAH concentrations progressively decreased with the direction of water flow

among sampling sites. For example, the PAH amount at site WZ1 was 17 times higher than downstream at site WZ10. Due to the wastewater effluents, which led to high organic carbon content, category WD contained relatively higher concentrations of PAH than categories WZ and WR. The concentration levels of  $\Sigma\text{PAH}$  remained at the same level at sites WD1, WD2, WBD3 and WD3, until they increased at site WAD3 (1,062  $\mu\text{g}/\text{kg}$  d.w.) which is located nearby point source pollution sites such as paper mill effluents. Then, the  $\Sigma\text{PAH}$  decreased again at sites WFD3 (859  $\mu\text{g}/\text{kg}$  d.w.) and WD4 (282  $\mu\text{g}/\text{kg}$  d.w.). Finally, after confluence point of WZ and WD categories, WR category showed a similar trend of  $\Sigma\text{PAH}$  concentrations along the sampling sites. They ranged over 111-288  $\mu\text{g}/\text{kg}$  d.w.

#### Profiles of PAH

The physical and chemical properties of PAHs are responsible for their mobility in the environment. The road runoff pollution by PAH contributed to the contamination of river sediments. 2-3 ring PAHs are accumulated and enriched more rapidly than 4-6 ring PAHs, especially in fine sand fraction [5]. Impacts of urban runoff on particulate metal concentrations during seasonal variation was studied at Seine River in France. The results have shown similar trends of metals for the runoff and the river waters [18]. These findings were supported by Kukkonen et al. and Fu et al. [8, 19]. Therefore, fresh sediment profiles which are dominated by 2-3 ring PAH could provide an indication of their source, especially to the street traffic and urban runoff.

The classification of the PAH results into 2-3 and 4-6 ring systems have shown the following facts concerning the sedimentation profiles: 1) the downstream area of

Zarqa River was dominated in both seasons by older sediment profiles (4-6 rings system). That might be explained as photo-degradation and volatilization processes for the small PAH amount found downstream considering that limited transport of PAHs during summer season. 2) Fresh sediment profiles, mostly containing 2-3 rings system, appeared after several rainfalls. That might be caused by the wash-out load of roads and residential areas, especially as Zarqa River is used to transport surface runoff of Amman area to King Talal Reservoir. Finally, the sediment texture from Zarqa River was dominated by sandy clay loam to sandy loam in both seasons. This might be the reason for the enrichment of PAHs in fine sandy and silt fractions, while clay fraction is always poor with PAH [5]. The profiles of PAHs along the investigated area for summer and winter seasons, respectively, are shown in Figures 4a and 4b. The distribution patterns of 16 PAH in the present work were in agreement with findings of Jiries [20] and Jiries et al. [21, 22], who studied these 16 PAHs in road dust as well as in rain water and runoff in Amman area.

The individual distribution of PAHs for summer season was in descending order: phenanthrene > pyrene > fluorene > naphthalene > fluoranthene > chrysene > anthracene > acenaphtene > benzo[g,h,j]perylene. Furthermore, mostly similar trends were observed also for winter season, the dominating PAHs in descending order were: phenanthrene > pyrene > fluorene > fluoranthene > chrysene > naphthalene > benzo[b]fluoranthene > acenaphtene > anthracene > benzo[g,h,j]perylene. However, the rest of PAH were detected below the limit of determination (10 µg/kg).

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