

Polycyclic aromatic hydrocarbon in rain and street runoff in Amman, Jordan

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Abstract: Concentrations of polycyclic aromatic hydrocarbons (PAHs) were determined in the rain and street runoff samples from two sites in the vicinity of Amman City during the pluvial period 1999–2000. The results showed that elevated levels of PAHs were detected in the city center (site 1) than the residential area (site 2) and that the levels were higher in street runoff than rain samples of the same sites.

The highest concentration of PAHs in both street runoff and rain samples were observed in the first rainy month (November 1999) which indicated a wash out effect of PAHs originating from vehicular emission accumulated during the long dry summer season before sampling. Within the investigated cold winter seasons, fluctuations in PAHs concentration were observed. The variation was attributed to the fossil combustion for heating purposes and to intervals between rainfalls: as the longer the intervals between rains were, the higher the PAH concentration were.

Removal of PAHs from the atmosphere through precipitation over the investigated period varied with time and places depending on the amount of rainfall where higher rainfall removed higher amount of PAHs from the atmosphere. The amount of PAHs washed out through precipitation was estimated to be around 14.8 mg/m² and 21.1 mg/m² for sites 1 and 2 respectively.

Keywords: PAHs; rain; street runoff; Jordan

Introduction

Various activities in urban areas such as traffic, domestic heating, biomass burning and others emit many pollutants into the atmosphere among which is a class of organic pollutants known as polycyclic aromatic hydrocarbon (PAHs). The environmental concern about these pollutants is due to its widespread occurrence and the documented carcinogenic and mutagenic activities of several of these compounds (Nielsen, 1996).

After these PAHs are emitted into the atmosphere, some are absorbed onto the particulate phase. Especially the nonvolatile compounds with five or more rings (Pitt, 1973; Bayona, 1988; Kiss, 2001) incorporate in street dust and finally settle to the ground by dry or wet deposition. However, the volatile compounds remain in the gaseous. PAHs with medium volatility distribute between gaseous and particulate phase (Vo-Dinh, 1989). Once emitted, they can either be transported a long distance in the atmosphere or reside in the environment for a long period unless they are removed either through transportation as surface runoff ending in the aquatic environment (Dannecker, 1990) or through microbiological degradation which is the major route through which PAHs are removed from contaminated environment beside other processes such as volatilization, chemical and photochemical reaction with other atmospheric gases such as O₃, NO_x and SO_x. Degradation of PAHs can produce compounds that can be more or less mutagenic and carcinogenic than the parent PAHs (Baek, 1991). Hoffmann *et al.* (Hoffmann, 1984) found that PAHs in urban runoff were similar in composition to those in atmospheric deposition. Takada *et al.* (Takada, 1990; 1991) found that PAHs in runoffs of heavily trafficked areas of Tokyo were mainly derived from automobile exhaust while those from residential streets were from other combustion products.

Street dust contamination with PAHs and heavy metals in various traffic activities in Amman was investigated (Jiries, 2002). He found that tunnels were the most polluted sites in the city. Jiries *et al.* (Jiries, 2001a) investigated heavy metals and the major ionic composition of street runoff in Amman. They

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found that vehicular activities are the main source of its chemical composition where high salinity and heavy metal content were found in the city center and the least were detected in the residential areas. The ionic composition of the atmosphere at high latitudes of Amman City was investigated through rainfall by Jaradat *et al.* (Jaradat, 1998) and near the earth surface through chemical composition of dew (Jiries, 2001b). They found that the content of heavy metals at city center sites was not higher than in residential areas through anthropogenic activities, the heavy metal content of dew was higher in winter than summer seasons and was attributed to higher use of fossil fuel combustion for heating purposes during cold winter seasons.

Rainfall and its street runoff quality are of vital importance in a semiarid country such as Jordan where the major source of fresh water in the country is the scarce amount of rainfall. As rainfall occurs it wash out the pollutants from the atmosphere to the ground where it meets PAHs accumulated on the streets, therefore street runoff generally contains elevated levels of PAHs, which adversely impact the water quality of both surface and groundwater.

1 Materials and methods

1.1 Study area

The area of investigation is located in the mountainous city of Amman, the capital city of Jordan, which was established at the beginning of the 20th century. A rapid growth of population took place that in the last few decades so that it covers an area of more than 160 km² with around two million inhabitants driving more than 200000 vehicles at present day.

Two sites were selected in the sampling area (Fig.1). Site 1 is located in the City center of Amman and is characterized by heavy traffic, whereas site 2 is located in a residential area in the northwestern part of Amman with a light to medium traffic density.

Under prevailing semiarid conditions, infiltration of storm water is considered the only source of groundwater recharge for the Amman-Zerka aquifer, which lies mainly under the City of Amman. The storm runoff percolates partially and rapidly into the highly fractured cretaceous limestone towards the aquifer below the City of Amman (Salameh, 2002). A high portion of the street runoff drains without pretreatment through the Zerka River and ends at the King Talal dam where its water is being used for agricultural purposes.

In Jordan, with its Mediterranean climate, rainfall occurs only in the winter season, from November to April; therefore, rainfall and sediments from street runoff samples were restricted to this period of the year. Although the two sites are less than 15 km apart, and the total rainfall for the investigated year ranged from 107 mm at site 1 to 236.0 mm at site 2 (Table 2). However, this was below the average annual rainfall for the area.

1.2 Chemicals

Acetonitrile and dichloromethane were HPLC grade (from Riedel de Haen Seelze, Germany and Aldrich Chemical Company respectively). Silica gel (100–200 mesh) was supplied by sigma (St. Louis,

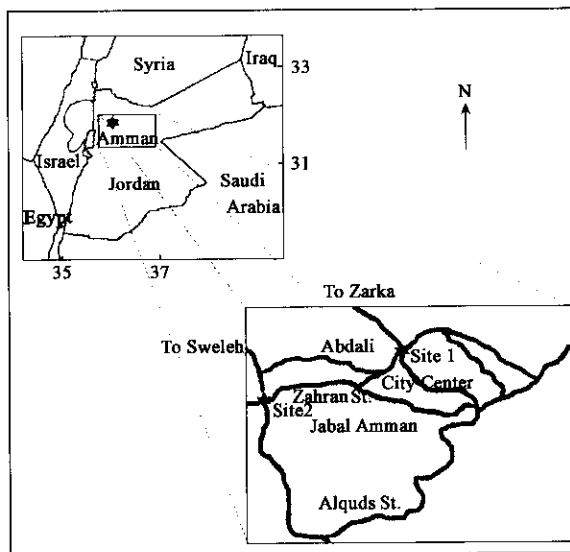


Fig.1 Location map

MO, USA). Unless otherwise stated all other solvents and chemicals were analytical grade in high purity available. Deionized water was performed using a Milli-Q plus system from Millipore (Molsheim, France).

1.3 Sample extraction and processing

Rain and street runoff water samples (200.0 ml) were extracted three times with a total of 150.0 ml dichloromethane in a separating funnel and the solvent was removed at 20°C and 14 mm mercury pressure to dryness. The residue was redissolved in 5.0 ml dichloromethane and cleaned by adsorption chromatography. The solvent was then evaporated in a rotary evaporator to almost dryness and 5.5 ml acetonitrile were added prior to analysis.

1 ml of the extract was diluted to 5.0 ml with acetonitrile followed by addition of 5.0 ml deionized water. The mixture was shaken, allowed to stand for 30 min at room temperature and finally filtered through a micro filter (0.2 μm , Brown-Rim-D) obtained from Schleicher & Schuell (Dassel, Germany). Aliquots of these samples were filled in auto sampler vials, 10 μl injected into the HPLC-system.

1.4 Analysis

The HPLC system used for analysis was HP series 1100 system (Hewlett Packard, Waldbronn, Germany) consisting of a vacuum degasser, a gradient pump, an auto sampler, a column thermostat, a diode array detector, a fluorescence detector and a computer workstation. The analytical column was a MZ-PAH, 250 \times 3 mm I.D (MZ Analysetechnik, Mainz, Germany). Injection volume was 10 μl and the flow velocity 0.5 ml/min. The separation gradient used for the separation of 16 PAHs at 33.7°C was as follows: Starting with 58% acetonitrile within 35 min the acetonitrile content increased to 100% acetonitrile where it was hold for 10 min. Within the next two minutes starting conditions (58% acetonitrile; 42% water) were reached and the column was equilibrated 13 min with these conditions. The native fluorescence of the PAHs was used for their detection and qualification. The analytical column was a Bakerbond PAH, 250 \times 3 mm I.D (Baker, Deventer, The Netherlands). Injection volume was 10 μl and the flow velocity 0.5 ml/min. The native fluorescence of the PAHs was used for their detection and qualification.

External calibration was used for quantification. A six-level-calibration standard solution of 16 PAHs and two internal standards in acetonitrile in the concentration range from 0.4–1000 $\text{pg}/\mu\text{l}$ was performed. The original solution of PAHs in acetonitrile was obtained from Promochem (Wesel, Germany).

The overall absolute recoveries of individual PAHs compounds were found to be better than 78% in most of the samples. Data presented here were corrected accordingly and obtained from the mean of duplicate analysis.

2 Results and discussion

Typical chromatograms of a standard solution and of an analyzed sediment sample are shown in Fig. 2, illustrating a good separation of the analytes of interest within less than 40 min.

Statistical analysis of the PAH concentrations and their mean sum in precipitation and street runoff samples from the two sites are summarized in Table 1. Throughout the investigated period total PAHs ranged from 60.5 to 974.8 ng/L and 46.1 to 290.6 ng/L for rainwater collected from sites 1 and 2 respectively. Street runoff concentrations of PAH ranged from 70.4 to 1420.8 ng/L and 65.9 to 490.9 ng/L for sites 1 and 2 respectively with predominant naphthalene in all samples. This can be attributed to higher accumulation of PAHs on streets than on airborne particulate due to accumulation of settled PAHs on streets during the dry summer season as well as other sources such as asphalt erosion. These results are higher than PAHs concentration reported in other humid cities such as Paris (Ollivon, 1999), which can be attributed to a higher washout through higher precipitation compared to the investigated area.

Fluctuation of all PAH concentrations within the sampling period may vary according to intensity and frequency of rainfall and sampling sites (Ollivon, 1999). Thus uneven distribution of rainfall events where

the particle bound PAHs from sealed surfaces such as streets are quickly exhausted and renewed contamination begins immediately afterwards (Krein, 2000).

Table 1 Statistical summary of PAH concentrations in ng/L in rain and street runoff samples collected from the investigated area

	Site 1						Site 2					
	Rain			Street runoff			Rain			Street runoff		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Naphthalene	11.4	132.2	63.61	11.2	433.7	116.53	13.2	125.2	51.09	14.2	247.6	63.4
Acenaphthene	0	0	0	0	0	0	0	0	0	1.9	1.9	1.9
Fluorane	0.4	6.7	2.22	0.4	31.4	7.5	0.3	1.7	1	1.7	7.6	3.88
Phenanthrene	7.2	78.3	23.59	4.5	141.4	36.63	4.2	20	10.13	3.6	45.8	23.67
Anthracene	1	26.5	6.04	1.7	16.7	6.22	0.6	4.6	2.45	2.4	3.8	3.1
Fluoranthene	2.8	164.3	33.6	8.2	131.3	36.33	3.4	31.7	14.61	2.8	46	23.09
Pyrene	7.3	233	47.83	16.8	186.3	55.83	5.9	41.1	18.31	12	53.5	27.27
Benz(a)anthracene	8.8	8.8	8.8	2.3	37.6	11.73	1.7	2.7	2.2	1.5	5.7	2.88
Chrysene	1.4	50.8	11.07	3.7	56.5	14.2	1.4	10.9	5.46	1.6	11.6	7.53
Benzo(e)pyrene	7.3	76.9	25.96	6.5	82.8	31.83	5.7	13.5	9.22	10.2	17.7	12.9
Benzo(b)fluoranthene	3.5	36.3	9.33	2.2	36.9	10.7	1.5	12.1	4.9	4.4	8.6	6.75
Benzo(k)fluoranthene	1.6	9.7	3.36	1.6	22.6	5.16	1.3	5	2.39	1.8	3.1	2.28
Benzo(a) pyrene	2.4	15.6	4.9	2	55.7	11.58	2.2	4.1	3.02	1.9	7.5	3.34
Dibenz(a,h)anthracene	0.9	2.6	1.33	0.9	6.8	3.38	1.4	1.4	1.4	1.3	1.3	1.3
Benzo(g,h,i)perylene	3	96	21.57	7.7	121	27.14	2.5	12.1	6.2	4	22.3	10.15
Indeno(1,2,3-cd)pyrene	1.5	37.1	7.74	0.7	60.1	14	0.8	4.5	2.05	0.6	6.9	2.58
Sum	60.5	974.8	270.9	70.4	1420.8	388.7	46.1	290.6	134.4	65.9	490.9	196.02

Although the concentrations of high molecular weight PAHs are expected to be higher in street runoff than in rain samples, elevated concentration levels were found in rain. This was attributed to the adsorption of these PAHs on air rich aerosols in the atmosphere. Especially the nonvolatile compounds with five or more rings would be absorbed onto the particulate phase (Bayona, 1988; Pitt, 1973; Kiss, 2001). In general the average concentrations of the total PAHs were 1.5–6.4 folds higher in street runoff compared to rainfall at the same period, however, higher enrichment was found in site 1 due to higher vehicular activities. This can be attributed to elevated levels of petroleum hydrocarbons such as asphalt from street erosion increasing the level of PAHs in street runoff.

In rain samples, high levels of heavy PAHs which are primarily in aerosol in the atmosphere were found together with the more volatile PAHs, as rain samples include both the gaseous and the particulate fraction

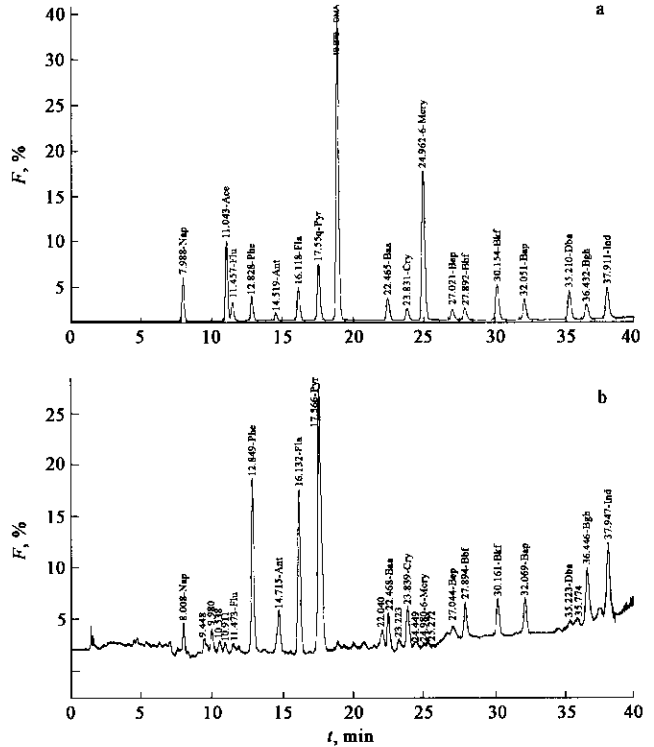


Fig.2 Typical chromatograms of the standard solutions (a) and one of the analyzed sediment samples (b)

of atmospheric PAHs. Ollivon *et al.* (Ollivon, 1999) reported similar results. Acenaphthene was not detected in any of the samples, which is due to its high fugacity (Krein, 2000).

To get an idea of the source of PAHs, the ratio of fluoranthene: pyrene was calculated in the rain and street runoff samples. The fluoranthene: pyrene ratio in most of the samples were predominantly contaminated by fossil fuel origin (e.g. refined petroleum product) as their ratio with a few exceptions, were less than 1 (Pham, 1999).

The renewed contaminants were also affected by fluctuation in temperature and fossil fuel combustion for heating purposes. Therefore, the highest concentrations were observed in the first sampling month, as the atmosphere and street were highly loaded with PAHs accumulated during the dry summer season decreasing with successive precipitations in addition to low amount of precipitation (around 1.1 and 4.4 mm for sites 1 and 2 respectively) and in cold winter months (January and February) where heating activities were at maximum use.

Several authors had reported that at least half of atmospheric PAHs were scavenged by rainy events (Hart, 1993; Masclet, 1986). The average amount of PAHs which scavenges from the atmosphere through precipitation during the sampling period was calculated according to the amount of rainfall and its PAHs concentration as using the following equation:

$$\text{PAHs removed/m}^2 = (\text{Concentration of PAHs in rain sample}) \times (\text{Amount of rainfall/m}^2).$$

The results shown in Table 2 indicate that the removed amount of PAHs from the atmosphere was proportional to the amount of rainfall. As the PAHs concentration is supposed to be higher at city center (site 1), the amount of PAHs removed from the atmosphere during the rainy period was higher at the residential area (site 2). These findings are confirmed by a highly significant correlation between amount of rainfall and the amount of PAHs removal ($r = 0.96$). These results might be attributed to the suggestion that the highest PAHs removal from the atmosphere occurred at the beginning of the rainy season at both site as the atmosphere was loaded with PAHs during the long dry summer season.

The first month of low rainfall removed the highest concentration of PAHs in both rain and street runoff samples. A sharp decrease in PAHs concentration was recorded after first this month of fluctuating PAH concentrations were observed in the following months as rainfall events and intervals between them were not uniform in amount and duration. The longer the period of dry days the higher PAH concentrations were observed in both rain and street runoff.

3 Conclusions

The present work illustrates a better understanding of the behavior of PAHs in rain and street runoff in a semiarid region where it is the main and only source for groundwater recharge in the area.

The most important factor controlling PAHs concentration in rain and street runoff samples are rainfall intensity and the intervals between rainfall events. Removal of PAHs from the atmosphere of Amman through wet precipitation ranged from 14.8 mg/m² at the city center area to 21.1 mg/m² at the residential area. The controlling factor was the amount of rainfall. In rain samples low molecular PAHs as well as high molecular PAHs were determined. Thus it can be assumed that in rain PAHs from both, the gaseous and the particulate fraction are collected.

Table 2 Average removal of total PAH in mg/m² from the atmosphere and the amount of rainfall during the sampling period

Month	Site 1		Site 2	
	Removal, mg/m ²	Rain, mm	Removal, mg/m ²	Rain, mm
November	0.2	4.4	0.070	1.1
December	0.527	4.4	1.477	7.8
January	12.566	85.6	10.216	86.8
February	0.79	8.1	6.857	100.1
March	0.244	3.4	1.889	31.7
April	0.088	1.1	0.595	8.5
Total	14.415	107	21.104	236

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