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DETERMINATION OF CARCINOGENIC POLYCYCLIC AROMATIC HYDROCARBONS IN AIR SAMPLES IN IRBID, NORTH JORDAN

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ABSTRACT

Air samples were collected at an urban site and a rural (BERQESH) site during February (2017) until March (2017) to determine concentrations of polycyclic aromatic hydrocarbons (PAHs) in Air. The extraction process was done by using Soxhlet apparatus and methylene chloride as solvent. The sample clean up step is performed by solid phase extraction. The analysis of PAHs samples are carried out by GC/MS. Low molecular weight PAHs dominated in all samples such as acenaphthylene, fluorene and anthracene, while high molecular weight PAHs was not detected. The total mean PAHs concentration in summer in Rural Area (92 ng/m^3) is higher than that in winter (46 ng/m^3). In addition, PAHs total mean concentration in the day time is higher than that in the night time. The total mean PAHs concentration in summer in Urban Area (124 ng/m^3) is higher than that in winter (75 ng/m^3).

Keywords: pollution; (PAHs); environment; fossil fuels; Jordan; human; season.

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1. INTRODUCTION

The exposure of human beings to environmental pollution can be traced back to their first appearance on earth. The attention toward polycyclic aromatic hydrocarbons (PAHs) started in the air toward the end of 18th century, after a link was suggested in 1775 between scrotal cancers which were undergone by chimney sweeps and the soot which they were exposed to. During that period, these composites were surely unidentified. It was finally confirmed in 1930s that the cancer-causing elements existing in the soot were PAHs [1].

1.1. Health Effect

Pollutants originating from industry such as domestic heating and gasoline and diesel engines contain compound chemical components including proven and potential carcinogens and mutagens [2-3]. Current studies established that airborne particulates particularly diesel exhaust particles constitute an essential health threat factor. Harmful effect of diesel exhaust particles comprises acute irritation of eyes and respiratory tracts, annoyance reaction and protracted diseases such as allergic nasal catarrh, cancer and asthma [2, 4]. Health related problems regarding certain PAHs are depicted in Table 1.

Table 1. Health effects of some PAHs

PAH	Health Effect
Acenaphthene	Annoying to eyes, skin and mucous membrane.
Anthracene	Skin damage and might irritate the respiratory tract.
Phenanthrene	Can cause photosensitization of skin.
Benzo(a) pyrene	Human carcinogen, connected with stomach tumors, lung tumors, and skin tumors.
Pyrene	A skin irritant.
Naphthalene	Irritating to skin, vapors can cause irritation to eye.

1.2. Research Objectives

Evaluations of urban air quality are intended to provide essential concentrations of atmosphere within the established levels. Therefore, this study provides information on the levels of PAHs for air quality assessment [11] in Irbid. The general objective of this study is to determine the levels of environmental pollution in Jordanian environment, particularly the

PAHs levels of air samples in Irbid, northern part of Jordan. The specific objectives of this study are to determine the pollution level of Polycyclic Aromatic Hydrocarbons, particularly environmental pollution levels in Jordanian environment in air.

2. METHODOLOGY

Irbid is study area is considered one of the largest Jordanian cities. It is situated north of the Jordanian capital-Amman by nearly 80 kilometers. Irbid is well-known for its enriched attractive plains which are occupied by different kinds of vegetables, peans and trees. Urban-site samples were collected from the rooftop of a three-story (10 meter height) building located in a diversified institutional, commercial and residential area in the Irbid city center. The rural-site samples were collected from the rooftop of a three-story building (10 meter height) located in Berqesh, which is 8 km north of Irbid city

2.1. Extraction of PAHs

Subsequent to final weighing, the filters were spiked with 20 pL of domestic standard of 2 ppm. The spiked filters and foams were then soaked in 150 mL dichloromethane in the soxhlet apparatus for two hours. Then, extraction commenced for no less than 10 hours, offering beyond the least 20 cycles necessary for thorough extraction. The extracts were finally concentrated to 1-3 mL in a rotary evaporator.

2.2. Sampling Program

The PAH samples in the urban and rural areas of Irbid city (BERQESH) were gathered between February 2017 and March 2017 as shown in the following Table 2.

Table 2. Sampling Information

Sampling Period	**Number of Samples**			
	Urban Area			**Rural Area**
	24 h	**12 h**	**4.30 h**	**24 h**
February, 2017	17	4	10	2
March, 2017	25	8	15	3

2.3. Analysis of Samples

Analysis was performed on a gas chromatograph (GC) (Varian, cp3 800) with mass spectrometer (MS) (Saturn 2000), which employs ultra-trace ion trap with a range of 10-650 mass unit using electron impact ionization mode. A DB-5.625 fused silica capillary column (Suppico, USA), 0.32 mm i. d., 30.0 m long and 0.25 jam film thickness (5%-phenyl-95% dimethyl polycycloxane) was used. The GC with helium (purity 99.99%) as a carrier gas comes with a 1079 general capillary injector, which offers five methods of injections.

2.3.1. Gas Chromatography (GC)

In gas chromatography, the sample is converted to the vapor state and the eluent is a gas (the carrier gas). The stationary phase is generally a nonvolatile liquid supported on an inert solid. The sample is rapidly injected by means of a hypodermic syringe through a rubber septum into the column. The sample injection port, column and detector are heated to temperatures at which the sample has a vapor pressure of at least 10 torr. The injection port and detector are usually kept somewhat warmer than the column to promote rapid vaporization of the injected sample and prevent sample condensation in the detector [5].

2.3.2. Gas Chromatography-Mass Spectrometry (GC-MS)

The appearance of a chromatographic peak at a particular retention time suggests, but does not guarantee the presence of a particular compound. Hence, confirmatory evidence is usually sought. A very powerful tool is the combination of gas chromatography with mass spectrometry, a technique known as Gas Chromatography-Mass Spectrometry (GC-MS) [5].

2.3.3. High-Performance Liquid Chromatography (HPLC)

Two criteria should be followed in order to reduce the circulation and the required time for the movement of sample elements to and from the interaction position in the column. First, porous storing materials as a provision for solid level with particle size of 3-10 im and great spherical regularity to enable optimal homogeneity and storing density and second, the fixed liquefied phase has to be in a thin identical film with no stationary pools [5]. HPLC apparatus contain four major portions; the column and detector, pump sample injection system and mobile-phase [6].

3. RESULTS AND DISCUSSION

3.1. Recoveries

Recoveries were assessed by using four different fiber filter papers spiked with 150 µL PAHs (100-2000 ppm) and 20 µL internal standard (500 ppm), 130 µL PAHs (100-2000 ppm) with 20 µL internal standard (500 ppm), 100 µL PAHs (100-2000 ppm) with 20 µL internal standard (500 ppm) and 80 µL PAHs (100-2000 ppm) with 40 µL internal standard (500 ppm) respectively. All recoveries were from 42-95, depending on PAHs species except for acenaphthene (42).

The overlap between peaks of acenaphthene-dl0 and acenaphthene might be the only reasonable explanation for the high recovery of acenaphthene. Table 3 represents the recoveries and relative standard deviation of our target compounds.

Table 3. Recoveries and relative standard deviation of PAHs compound.

PAH Species	% Recovery (% RSD)
Acenaphthylene	95
Acenaphthene	41
Fluorene	42
Anthracene	68
Phenanthrene	57

3.2. Detection Limit

A solution was prepared by mixing 100 µL of standard PAHs solution and 100 µL CH2C12, then dilution of 1 µL from the prepared solution to 2 mL. The final solution was used to determine the detection limit of our compounds. Detection limits (S/N = 3) are tabulated and all of them are less than 86 ng Table 4.

Table 4. Detection limits of PAHs compound

PAH Species	Detection Limit (ng)
Acenaphthylene	86
Acenaphthene	12
Fluorene	15
Anthracene	5
Phenanthrene	11

3.3. Determination of PAHs

To determine the concentration of PAHs in our study area of samples were collected, samples collected for 24 hours.

3.4. PAHs in 24-Hour Samples

To determine the concentrations of PAHs, 43 samples of the first type were collected (24 hours). 38 samples of PAHs were taking in Urban Area and 5 samples (s1, s5, s8, s27, s40) were taking in Rural Area during summer and winter season. The aim of these samples is to compare between urban and rural areas and to find the highest concentration PAHs during summer and winter season. The highest percentage of PAHs was found during two seasons in Urban Area 199 ng/m^3 and the highest percentage of PAHs was found in Rural Area 154 ng/m^3.

Table 5 and 6 show the results for the determination of three PAHs in 24-hour samples. Low molecular weight (contain three rings or fewer) PAHs are dominant in all samples, while high molecular weight PAHs are not detected. Low molecular weight PAHs compound usually exist in high concentration in diesel exhaust particulates, while high molecular ones are not available, this might explain our results.

There are major differences in PAHs concentration between warm and cold seasons. The comparison of summer and winter data will be done by using samples collected for 24 hours. Table 5 and 6 represent the range and means concentration (in ng/m^3) of our target PAHs compound.

Table 5. PAHs concentration at Urban Area in summer, winter seasons (in ng/m^3)

PAHs Species	Winter Range	Mean	Summer Range	Mean
Acenaphthylene	6-96	51	6-181	93
Fluorene	2-18	10	2-38	20
Anthracene	1-26	14	1-20	11
Total		75		124

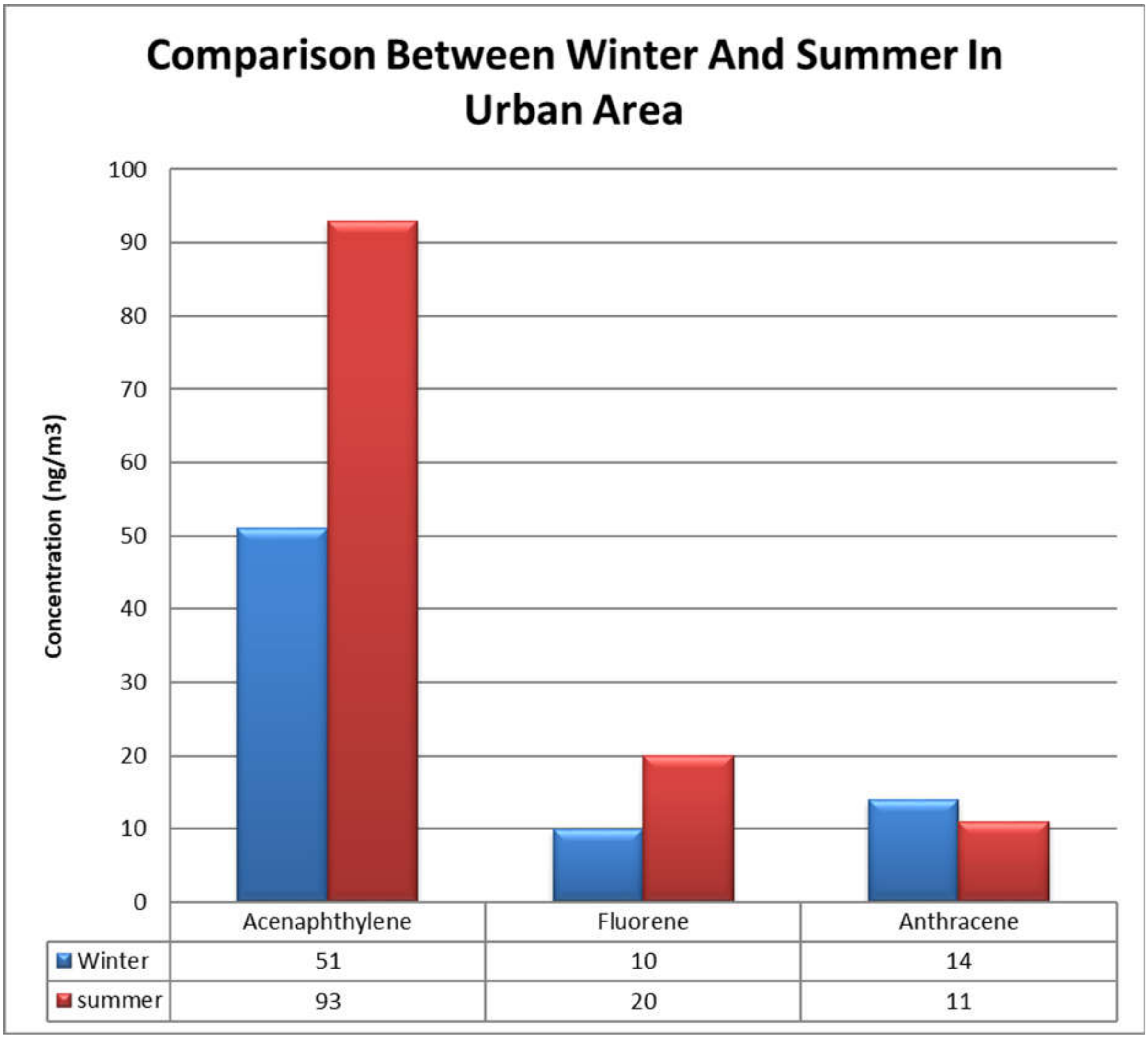
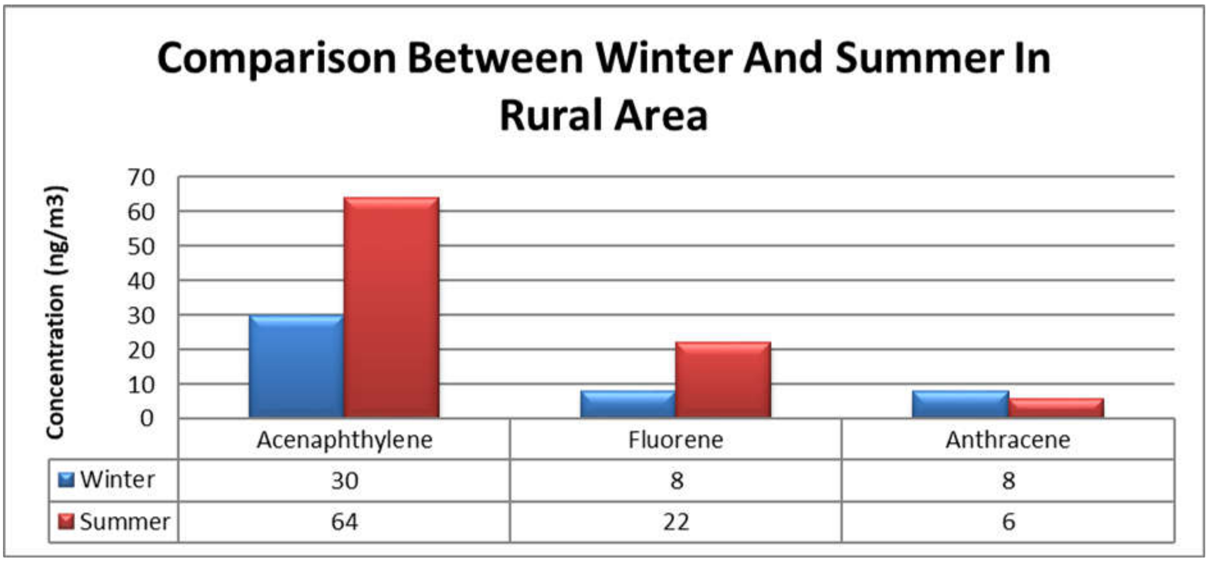


Fig.1. Comparison between winter and summer season in Urban Area

In Fig. 1, we see that the concentration of Bahs in the air in the summer is more than in the winter because many sources of this pollution [9-10] are very active and active due to many active activities in the summer. Unlike the winter where the number of cars on the streets and the number of workers in factories, leading to a low concentration in the air with increased sources (Bahs) in the summer.

Table 6. PAHs concentration at Rural Area in summer and winter seasons (in ng/m^3)

PAHs Species	Winter Range	Mean	Summer Range	Mean
Acenaphthylene	4-108	30	41-86	64
Fluorene	1-18	8	20-25	22
Anthracene	16-29	8	6-6	6
Total		46		92



	Acenaphthylene	Fluorene	Anthracene
🟦 Winter	30	8	8
🟥 Summer	64	22	6

Fig.2. Comparison between winter and summer season in Rural Area

Normally, the concentrations of PAHs are higher in summer than in winter time due to increased coal and oil burning in summer [7-8].

Results in Fig. 2 show that the total means PAHs for samples in summer were higher than that in winter in Urban and Rural Area. This is due to the mild weather which increases the proportion of work and production in factories and increases the motor ratio, and thus leads to the activity of the population that would occur in an active movement in the commercial markets that produce PAHs. These are all contributing factors in the increase PAHs and all this increases the concentration PAHs in the air.

In winter either place an inactive season and most of the people sitting in their homes, resulting in a few hours of work in a few factories and move a few of the cars that produce a large proportion of PAHs, sets the burning of less fuel and oil and all this reduces the proportion PAHs in the air.

4. CONCLUSION

Low molecular weight PAHs especially acenaphthylene, fluorene and anthracene were dominant in all collected samples while high molecular weight PAHs were not detected. The PAH concentrations at urban site were higher than those at rural site due to the fact that large number of cars were passing through the urban site. The highest average PAHs concentration was found between 4.00 pm and 1.30 am, due to low temperature and decreasing photochemical reaction. PAH concentrations in summer (March) were higher than those in winter (February). There was a relation between PAH concentrations and meteorological variables such as wind direction, wind speed and temperature.

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