

## Environmental Assessment of Polycyclic Aromatic Hydrocarbon Concentrations in Air at Thermal South Power Station of Baghdad

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### Abstract

Sixteen polycyclic aromatic hydrocarbons (PAHs) concentrations were measured in aerosol samples collected for the period from April 2012 to February 2013 at thermal south power station of Baghdad. Fourty one aerosol sample were extracted with (1:1) dichloromethane and methanol using soxhlet for seventeen hour. The extraction solution was analyzed applying GC/MS. The PAH concentrations outside thermal south power station were higher than those inside it, and higher in summer season than in winter. Naphthalene, pyrene, Anthracene, Indeno [1, 2, 3-cd] pyrene and Phenanthrene were the most abundant PAHs detected in all points at the site sampling. The total polycyclic aromatic hydrocarbon (TPAH) and total suspended particles (TSP) concentrations were measured during the measurement period. For individual PAH compounds, the results showed a strong correlation with each other (0.998 - 0.77) at both sites.

**Keywords:** PAHs in air, toxic PAHs, analysis PAH by GC-MS.

### Introduction

Polycyclic aromatic hydrocarbons (PAHs) form a complex class of organic compounds containing two or more fused aromatic rings, and only carbon and hydrogen atoms. The physical and chemical properties of PAHs are determined by their conjugated  $\pi$ -electron systems, which are dependent on the number of aromatic rings and the molecular shape. The smallest member of the PAH family is naphthalene, a two-ring compound, which is found in the vapour phase in the atmosphere. Three to five ring-PAHs compounds are found in both the vapour and particulate phases in air [1].

PAHs cause mutagenic and carcinogenic activities of the metabolites of several PAH compounds. The studies showed that individuals exposed by breathing or skin contact for long periods to mixtures that contain PAHs can develop cancer [2-4].

In the atmosphere, PAHs compounds are released as a complex mixture of compounds due to incomplete combustion of organic matter, emitted from wood burning heaters, agricultural waste burning, motor vehicle exhaust, cigarette smoke, asphalt road and roofing operations. PAHs are widespread contaminants of the environment and a number of them

are either known or suspected carcinogens. Benzo (a) pyrene, a widely reported five-ring PAH, is known for its carcinogenic potency [5].

Natural emission sources of PAHs into the atmosphere include emissions from forests fires and volcanoes. Some of the PAHs are produced for commercial use; these include naphthalene, fluorene, anthracene, phenanthrene, fluoranthene and pyrene [6].

Sensitive, rapid and accurate methods were developed to determine PAHs in atmospheric particles. As highly efficient separation tools, GC-MS and HPLC were used for analysing them [7].

In this study, aerosol samples were collected from thermal south power station of Baghdad at two locations, inside the station close to the emission of PAHs and outside the station located at urban area surrounding the site. Sixteen PAHs were determined and analyzed by GC/MS.

## **Experimental Procedure**

### **1. Chemicals and Standard Materials**

Methanol and dichloromethane (Fluka, 99.8%) were used for extraction of PAH compounds. The standard individual PAHs (Naphthalene, Acenaphthylene, Acenaphth-ene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz(a)anthracene, Chr -ysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Dibenz(a,h)anthracene, Benzo(ghi)perylene and Indeno(1,2,3-cd)pyrene) were supplied by Dr. Ehrenstorfer company (Germany) with (99.9%) purity. These compounds (mixtures or single component) are soluble in acetonitrile or methanol.

### **2. Sampling and Samples Extraction**

Aerosol samples were collected using a low volume air sampler (RADECO, Inc., England), which was equipped with cellulose fiber filter.

Cellulose filters (4.5 cm diameter, 55mm thickness from Schleicher and Schuell, W. - Germany) were pre-heated at 70 °C for 45 min prior to use to reduce their water content. Before and after sampling, the cellulose filters were weighted on an electronic balance to determine the total suspended particles (TSP) and stored at low temperature in proper container until further extraction and analysis [8].

Fourty one sample were collected during measurement period. Sampling was done inside and outside the site twice a month for a period of 1.5 hour in the morning and evening using sniffer device (low volume air sampler). The samples were collected applying (2.0 - 4.0) m above ground. The ambient temperature, relative humidity (VAISALA model HM1, Finland) and wind rate (Lambrech, England) were measured during the measurement period.

After sampling polycyclic aromatic hydrocarbon were extracted in order to determine their concentrations in air samples by soxhlet apparatus using two solvents methanol and dichloromethane (1:1). Soxhlet extraction was performed for 17 h. The soxhlet extractor consisted of a 250 ml round-bottom flask, 50 ml extractor and condenser with water bath; this arrangement enabled the extraction of only one filter sample at time [9, 10].

The solvents were removed to dryness using a rotary evaporator (Yamato RE 510) at 60°C under gentle vacuum. The dried samples were dissolved in 5 mL methanol and the solution filtered in the micro filter (0.22 µm, Minisart, Sartorius Stedim Biotech GmbH 37070 Goettingen,

Germany) was put in glass container and kept at low temperature.

### 3. Standard Solution

The retention time of the individual compounds (PAHs) was measured with range concentration (3-334)  $\mu\text{g/L}$  in solvent. For the measurements, a 4-point calibration range is used for all PAH. The calibration ranges used are as follow: (3.33, 36.472, 67.412, and 334.215)  $\mu\text{g/L}$  in solvent.

The target compounds PAHs were identified by comparing the retention times and the mass spectra at the Technology University Darmstadt (TUD) in Germany. The final concentrations of compounds PAHs were calculated from calibration curve and converted to nanogram/ $\text{m}^3$  in air [11].

### 4. GC/MS Analysis

The analyses were performed using a GC-MS system (Agilent Technologies 5975C Series GC/MSD, USA) comprising a ChemStation software and Auto-sampler with Triple -Axis Detector. Gas chromatography (GC) was equipped with a flame ionization detector (FID). Separations were carried out using a Zebtron Guardian, phase:ZB-5MS, a non-polar, packed with 5% phenyl methylsilox. Capillary column was (L 30m  $\times$  I.D. 0.25mm  $\times$  df. 0.25 $\mu\text{m}$ ). Helium (99.99%) was used as carrier gas at a constant flow of 1.0  $\text{mL min}^{-1}$ . The temperatures of the MSD ion source and quadrupole analyzer were kept at 230 $^{\circ}\text{C}$  and 150 $^{\circ}\text{C}$ , respectively. The detection limit was 1 nanogram/ liter. The injected volume was 1  $\mu\text{l}$  in splitless mode.

The GC temperature program for PAH analysis ranged from 75 $^{\circ}\text{C}$  (hold for 3 min) to 235 $^{\circ}\text{C}$  (20 $^{\circ}\text{C}/\text{min}$ , hold for 18min), then ramped to 300 $^{\circ}\text{C}$  (15 $^{\circ}\text{C}/\text{min}$ , hold for 8 min) and the final temperature was 320 $^{\circ}\text{C}$ . The analysis time per sample was 43min [12-13].

### 5. Statistical Analysis

Statistical analysis including Pearson correlation analysis was performed using Statistical Package for Social Scientist (SPSS) version 19, and Microsoft Excel program. SPSS is a comprehensive system for analyzing data. SPSS can take data from almost any type of file and use them to generate tabulated reports, charts, and plots of distributions and trends, descriptive statistics, and complex statistical analysis.

SPSS has scores of statistical and mathematical functions, scores statistical procedures, and a very flexible data handling capability. There are many functions such as Descriptive Statistics, Contingency tables, Reliability tests, Pearson Correlation, T-tests and ANOVA. Pearson correlation regression techniques reflect the strength of association between continues variables [14].

### Result and Discussion

Fourty one sample were collected and quantified for sixteen PAH compounds by GC/MS device. A single target compound compared with retention time (RT) of individual standard PAHs compounds is given in Table 1.

The arithmetic mean and standard deviation of individual PAH concentrations in inside and outside of south station in two different seasons are given in Tables 2a and 2b. In summer season, the more abundance compounds were naphthalene, pyrene and Anthracene (1573.5, 203.0, 127.850)  $\text{ng}/\text{m}^3$ , respectively, while naphthalene and Indeno[1,2,3-cd]pyrene and Phenanthrene were in winter season (36.6, 13.003,10.08)  $\text{ng}/\text{m}^3$ , respectively. The highest concentrations of atmospheric PAHs was found in the urban environment (outside) as illustrated in Tables 2a and 2b, due to the increasing emission from south power station of

Baghdad: gas, vehicular traffic and slow dispersion of atmospheric pollutants. Fig. 1 shows the variation in the individual PAH concentrations.

Table 1: Retention time of individual standard PAHs compounds

No.	PAHs / Abbreviation	RT min.
1	Naphthalene (Naph)	8.38
2	Acenaphthylene (Acy )	10.42
3	Acenaphthene (Ace)	10.66
4	Fluorene (Flu )	11.30
5	Phenanthrene (Phe)	12.62
6	Anthracene (Ant )	12.70
7	Fluoranthene (Flt)	15.18
8	Pyrene (Pyr)	15.90
9	Benzo(a) Anthracene (B[a]A)	22.54
10	Chrysene (Chry)	22.79
11	Benzo(b) Fluoranthene (B[b]F)	32.45
12	Benzo(k) Fluoranthene (B[k]F )	32.58
13	Benzo(a) Pyrene (B[a]P)	33.71
14	Indeno(1,2,3-cd) Pyrene (Ind(cd)P)	37.93
15	Dibenzo(a,h) anthracene (dBA)	38.12
16	Benzo(g,h,i) Perylene (BghiP)	39.02

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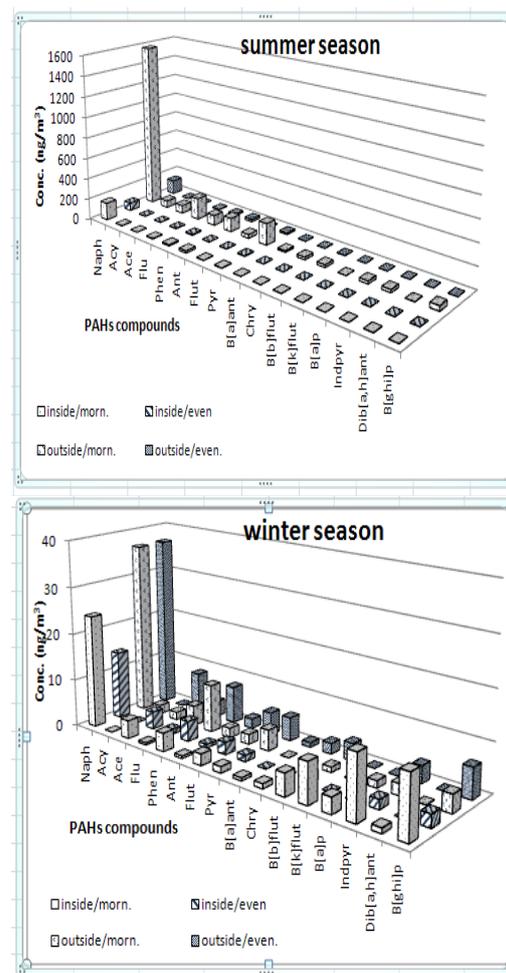


Fig. 1: Distribution of individual PAH concentrations

Average total polycyclic aromatic hydrocarbon concentrations (TPAH) and average total suspended particles (TSP) were measured during the period. Various environmental factors, including humidity, temperature and wind rate were monitored in sites four times and the average was taken. Spring season had high concentrations of TPAH (2847.62) ng/m<sup>3</sup>, while summer season had a high concentrations of TSP (3156.21) µg/m<sup>3</sup>. In winter and summer seasons, temperature ranged between (15.62-45.58) °C, while humidity ranged between (62.00-14.59). Table (3) shows values of TPAH, TSP and meteorological conditio

Table 2a: Average concentrations of individual PAHs (ng/m<sup>3</sup>) in summer season

Compounds	Inside/morning		Inside /evening		Outside/morning		Outside/evening	
	Mean (n=3)	SD	Mean (n=3)	SD	Mean (n=3)	SD	Mean (n=3)	SD
Naphthalene	163.185	3.815	72.580	2.920	1573.500	8.000	133.450	5.850
Acenaphthylene	1.900	0.100	1.045	0.055	64.850	0.850	1.250	0.050
Acenaphthene	0.995	0.005	0.650	0.050	76.005	3.505	1.700	0.100
Fluorene	3.900	0.100	3.500	0.100	203.750	3.050	3.6500	0.100
Phenanthrene	10.500	0.500	6.600	1.100	94.685	3.685	13.250	0.750
Anthracene	19.500	0.500	1.095	0.105	127.850	3.850	23.300	0.300
Fluoranthene	1.900	0.100	1.800	0.100	35.240	1.760	5.500	0.200
Pyrene	2.800	0.200	5.250	0.350	203.000	3.100	14.500	1.700
Benz[a]anthracene	0	0	0.150	0.050	14.500	0.500	1.150	0.150
Chrysene	0	0	0.530	0.010	23.250	1.750	1.050	0.050
Benzo[b]fluoranthene	0.950	0.050	0.585	0.015	24.250	0.750	0.850	0.050
Benzo[k]fluoranthene	0	0	0	0	0	0	0	0
Benzo[a]pyrene	0	0	0	0	25.900	0.900	0	0
Indeno[1,2,3-cd]pyrene	0	0	0	0	26.600	1.600	0	0
Dibenz[a,h]anthracene	0	0	0	0	0	0	0	0
Benzo[ghi]perylene	0	0	0.585	0.015	45.350	2.350	0.350	0.050

Table 2b: Average concentrations of individual PAHs (ng/m<sup>3</sup>) in winter season

Compounds	Inside/morning		Inside /evening		Outside/morning		Outside/evening	
	Mean (n=3)	SD	Mean (n=3)	SD	Mean (n=3)	SD	Mean (n=3)	SD
Naphthalene	23.947	1.017	14.387	2.564	36.605	0.805	36.650	0.497
Acenaphthylene	0	0	0	0	1.886	0.013	0	0
Acenaphthene	3.792	0.142	3.657	0.050	1.599	0.002	8.427	0.446
Fluorene	0.425	0.033	1.107	0.082	4.251	0.391	3.274	0.094
Phenanthrene	3.865	0.065	4.211	0.394	10.018	0.089	7.780	0.602
Anthracene	0.512	0.012	0.725	0.065	2.045	0.055	1.978	0.176
Fluoranthene	2.399	0.056	2.537	0.006	2.067	0.069	4.628	0.225
Pyrene	1.327	0.051	1.300	0.081	4.370	0.371	4.883	0.249
Benz[a]anthracene	0.614	0.003	0	0	0	0	0.950	0.050
Chrysene	1.005	0.005	0	0	0	0	2.2165	0.226
Benzo[b]fluoranthene	4.639	0.139	2.081	0.091	1.070	0.080	3.603	0.213
Benzo[k]fluoranthene	8.332	0.342	0	0	0	0	0	0
Benzo[a]pyrene	3.27	0.37	0	0	1.4305	0.0405	0	0
Indeno[1,2,3-cd]pyrene	13.003	2.003	1.935	0.055	2.330	0.220	3.529	0.139
Dibenz[a,h]anthracene	1.057	0.067	0	0	0	0	0	0
Benzo[ghi]perylene	12.519	2.619	2.589	0.101	3.652	0.102	6.254	0.264

Table 3: Meteorological conditions for all season and average concentrations of TSP and TPAH

season	Location	Time*	Temp °C	Hum. %	Wind rate m/s	Tsp µg/m <sup>3</sup>	TPAHs ng/m <sup>3</sup>
Spring	Inside	M.	34.055	25.47	0.70	226.2	1089.2
		E.	33.32	24.95	1.00	244.0	2847.6
	outside	M.	33.28	27.76	2.90	211.6	494.86
		E.	35.69	21.03	1.35	312.3	319.12
Summer	Inside	M.	42.22	16.60	0.70	3156.2	148.35
		E.	45.58	14.59	1.15	437.2	66.60
	outside	M.	38.34	20.23	1.70	931.7	2540.3
		E.	44.48	16.34	2.15	2812.6	134.7
Autumn	Inside	M.	34.17	27.08	1.00	1013.6	24.94
		E.	36.17	22.88	0.80	1156.9	17.47
	outside	M.	29.87	34.07	0.85	1724.4	278.92
		E.	35.31	23.70	1.65	1139.3	49.07
Winter	Inside	M.	21.84	43.37	0.95	409.7	47.85
		E.	22.22	39.13	1.95	355.2	26.77
	outside	M.	15.62	62.00	0.55	375.2	63.00
		E.	23.08	36.58	1.25	416.6	70.59

\*M: morning, E: evening

Table 4: Pearson correlation coefficients between the individual PAH compounds

Compounds	Naph	Acy	Ace	Flu	Phen	Ant	Flut	Pyr
Naph	1							
Acy	.870**	1						
Ace	.793**	.983**	1					
Flu	.892**	.998**	.974**	1				
Phen	.955**	.929**	.862**	.950**	1			
Ant	.457	.096	-.051	.155	.453	1		
Flut	.937**	.952**	.902**	.970**	.994**	.379	1	
Pyr	.954**	.926**	.857**	.947**	.999**	.458	.994**	1
B[a]ant	.937**	.819**	.732**	.847**	.944**	.566*	.932**	.948**
Chry	.875**	.982**	.962**	.985**	.937**	.161	.964**	.936**
B[b]flut	.608*	.665**	.659**	.664**	.614*	.059	.655**	.618*
B[k]flut	-.138	-.116	-.096	-.126	-.168	-.149	-.131	-.163
B[a]p	.607*	.829**	.870**	.812**	.665**	-.199	.729**	.663**
Indpyr	.259	.404	.444	.388	.274	-.218	.336	.275
Dib [a,h]ant	-.121	-.143	-.116	-.148	-.171	-.109	-.132	-.166
B[ghi]p	.562*	.757**	.794**	.740**	.601*	-.196	.663**	.599*

Continue to table 4

Compounds	B[a]ant	Chry	B[b]flut	B[k]flut	B[a]p	Indpyr	Dib[a,h]ant	B[ghi]p
B[a]ant	1							
Chry	.879**	1	.					
B[b]flut	.743**	.770**	1					
B[k]flut	.090	.029	.636**	1				
B[a]p	.649**	.871**	.881**	.379	1			
Indpyr	.426	.522*	.908**	.841**	.809**	1		
Dib[a,h]ant	.088	.004	.612*	.966**	.370	.805**	1	
B[ghi]p	.637**	.823**	.932**	.521*	.974**	.895**	.480	1

\*\* correlation at 99% confidence level.

\* correlation at 95% confidence level.

From Table 3, it can be seen that the concentrations of TSP and TPAH in winter period are less than the other periods, and this is due to heavy rain during winter period.

Statistical tools were applied to the PAH variables (Naph, Acy, Ace, Flu, Ant, Phe, Flut, Pyr, BaA, Chry, BbF, BkF, BaP, IcdP, DahA and BghiP) [15].

From the results of Table 4, individual PAH compounds showed strong correlation with each other (0.998 - 0.77), due to a similar source of PAH compounds emissions. The major source was incomplete combustion of fuel in the station and vehicle emission on the highway near the location of measurements.

Anthracene showed a negative correlation with other compounds as well as Benzo[k]fluoranthene as illustrated in Table 4.

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