ESTIMATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH's) PRESENT IN THE ATMOSPHERE OF URBANIZED REGION BADAMI BAGH IN LAHORE, PAKISTAN

I. Kalim[1, 2]*, N. Zahra[2], T. Fazeelat[1]

[1]Department of Chemistry, University of Engineering and Technology, Lahore, Pakistan
[2]Pakistan Council of Scientific and Industrial Research Laboratories Complex, Ferozepur Road, Lahore-54600, Pakistan
* Corresponding Author Email: ikalim@hotmail.com

ABSTRACT: The emerging mega city of Lahore has been progressing by leaps and bounds in last two decades which is directly related to an immense increase of number of vehicles and power generation systems using fossil fuels. The present study entails the quantification and evaluation of potential risk due to Polycyclic Aromatic Hydrocarbons (PAHs) which is one of the known organic pollutants from vehicular, power generation system's exhaust and other industrial activities. The samples of Total Suspended Particulate Matters (TSPM) were collected from various urbanized sites present at Badami Bagh, Lahore, Pakistan for the estimation of polycyclic aromatic hydrocarbons. The technique used for quantification of PAH's was Gas Chromatography. The concentration of mean total of PAH was 746.60 ng/m^3. Dibenzo(a,h) Anthracene was found to be in highest concentration of 142.35 ng/m^3 among all the polycyclic aromatic hydrocarbons under investigation.

Keywords: Polycyclic Aromatic Hydrocarbon (PAHs), Total Suspended Particulate Matter (TSPMs), Gas Chromatography, Organic Pollutant

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INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are comprised of many environmental contaminants that are basically denoted as a group of organic compounds and are commonly present in the atmosphere. The most familiar sources responsible for the production of polycyclic aromatic hydrocarbons includes the pyrolysis and incomplete combustion of organic matter such as wood, coal, oil as well as the fuels like petrol and diesel (Golomb *et al.,* 2001; Halsall *et al.,* 2001 and Garban *et al.,* 2002). Some of polycyclic aromatic hydrocarbons are formed through the pyrolysis of some very simple hydrocarbons like styrene, butadiene, n-butyl benzene, tetralin, and acetylene at a temperature of 700°C. As a result, the aromatic hydrocarbons produced from this process of pyrolysis include benzo[k]fluoranthene, benzo[a]pyrene, and benzo[b]fluoranthene (Knize *et al.,* 1999).

Of many structural type organic compounds, aromatic ring systems remain stable up to the temperature of pyrolysis (700°C) whereas, aliphatic compounds with C-H and C-C bonds break into free radical molecular fragments quite readily which are further subjected to recombination (Golomb *et al*., 2001 and Hwang *et al*., 2003). Up till now, around 30 compounds and many other derivatives of polycyclic aromatic hydrocarbons have been discovered having carcinogenic and mutagenic properties which make them largest class of carcinogens ever known (Bjorseth and Ramdahl, 1985). The environmental behaviour of the polycyclic aromatic hydrocarbons is generally determined by the physiochemical properties. At the atmospheric conditions they are found to be semi volatile constituents that are either in the form of vapours or adhered to some particles depending on what the vapour phase of the polycyclic aromatic hydrocarbons is (Wingfors *et al.,* 2001 and Basheer *et al.,* 2003).

Those polycyclic aromatic hydrocarbons which have low molecular weight with two to three fused rings are more volatile, water soluble, and are mostly found in vapour phase, whereas, polycyclic aromatic hydrocarbons with high molecular weight have many fused rings and are found adhered with the particles (Smith *et al*., 1996).

Polycyclic aromatic hydrocarbons are not only found in urbanized industrial regions but also in rural also (Gevao *et al.,* 2000 and Garban *et al.,* 2002) and remote areas (Kallenborn *et al.,* 1998 and Migaszewski, 1999) for the reason that they get easily transported over long distances and persist in the environment (Aamot *et al.,* 1996 and Halsall *et al.,* 1994). These are near the source of emission where higher intensities of site specific polycyclic aromatic hydrocarbons are found. Many environmental samples like atmospheric particles have been studied for PAH in the last few years (Aamot *et al.,* 1996 and Halsall *et al.,* 2001). A very small amount of data has been acquired from the underdeveloped countries. India has previously produced its data on PAH concentration to study the carcinogenic effects through the samples obtained from the atmospheres of urbanized

areas in Lucknow (Bhargava *et al.,* 2004), Mumbai (Mohan *et al*., 1983 and Kulkarni and Venkataraman, 2000), Nagpur (Vaishali, 1997), and Ahmedabad (Agarwal *et al.,* 1982 and Raiyani *et al.,* 1993). There was quite a difference found in the values obtained from the residential and industrial zones in Ahmedabad. Residential area had about 23 to 66ng m^{-3}, whereas, the industrial site had double the levels of concentration i.e. 90 to 195ng m^{-3}. The concentrations of four different types of polycyclic aromatic hydrocarbons in the industrial area of Mumbai were found to be 20 to 95ng m^{-3} (Pandit *et al.,* 1996).

The concentration of PAH measured in the commercial, industrial, and residential zones in Nagpur ranged from 125 to 195ng m^{-3} in which 70% of them were found adhered to the particles of 10µm diameter size (Vaishali *et al.,* 1997). The total average concentration of polycyclic aromatic hydrocarbons was estimated in winter season for the consecutive three years 1992, 1993, and 1994 which came out to be 77.40±21.16ng m^{-3}(Chattopadhyay *et al.,* 1998). Many studies have also been conducted indoor to observe the difference between the levels of polycyclic aromatic hydrocarbons in different areas.

The concentration of PAH in the indoor areas in Lucknow were found to be particularly high 2.23 to 46.07µg m^{-3} due to the combustion of cow dung but low 0.86 to 4.76µg m^{-3} from the combustion of liquefied petroleum gas or LPG (Bhargava *et al.,* 2004). There was higher concentration of polycyclic aromatic hydrocarbons in the breathing zones of Mumbai which elevated more in winter season as compared to the summer season (Kulkarni and Venkataraman, 2000).

The Profile of PAH concentrations in selected cities showed that the rural areas were subjugated by pyrogenic release of PAHs, while the road traffic is the major contributor of PAH increase in urban areas of Pakistan (Atif *et al*., 2015). The concentrations of PAHs are also higher than in U.K. samples, and, given the difference in ambient temperature, vapour-to-particle ratios of PAH are expected to be far higher in the hotter climate of Lahore (Smith *et al*., 1996).

Automobiles, industrial oil combustion, and cooking fuel combustion are the chief source of primary polycyclic aromatic hydrocarbons which gives way to the abundant non-volatile PAH of fine mode and the semi volatile PAH of the coarse mode (Kulkarni and Venkataraman, 2000). Many emission sources, factors causing PAH production, and the seasonal level variations at different locations have also been discovered in liaison to the persistence of higher levels of PAH (NEERI, 2006; Gupta *et al*., 2006).

Since there is hardly any data available on PAH in Lahore, Pakistan, the purpose of this research based study was to acquire the useful foundational information regarding the concentration of polycyclic aromatic hydrocarbon present in the total suspended particulate matter.

MATERIALS AND METHODS

The air samples were collected from Badami Bagh: the busiest area located in north of Lahore with the help of high volume samplers with 99% efficiency on the Whatman GFA Glass fibre filters (National Academy of Sciences, 1973). The height of 3m above level of the ground and time period of collection was selected for samples collection. Before sampling, acetone was impregnated on the glass fibres for the removal of any organic compound. These glass fibres were properly stored in the desiccators until sampling was carried out.

The filters used were cleaned by dichloromethane. The particulate matter concentrations ie TSP, PM_{10}, and $PM_{2.5}$ were obtained by drying and weighing the filters. Before analysis, these filters were stored in the dark. The extraction of PAH was done by using dichloromethane/n-hexane with the ratio of 1:1 and volume 10ml. It was further fractionated with the help of column chromatography and 20ml of dichloromethane/n-hexane of 1:1 was used for the elution. Samples were extracted with toluene using ultra sonic bath for about 30 minutes and repeated thrice for complete extraction. Alternatively sample were extracted using soxhlet extraction apparatus for about 8 hours.

Extracted samples were concentrated using rotary evaporator and further cleaned with cyclohexane using silica gel column chromatography and finally analyzed as per method (Dilip, 2003) on gas chromatograph (GC) using capillary column (HP-Ultra-2, 30 m) and flame ionization detector (FID). One-way analysis of variance (ANOVA) was applied using SPSS 17.0 for Windows (IBM SPSS Statistics 19). The mean values were obtained by statistical analysis for each PAH (Kalim *et al.,* 2015).

RESULTS AND DISCUSSION

Gas Chromatographic technique was used to quantify 16 PAH's in collected sample at Badami Bagh. Sixteen PAHs and related compounds in sample obtained from Badami Bagh are shown as in Figure 1.

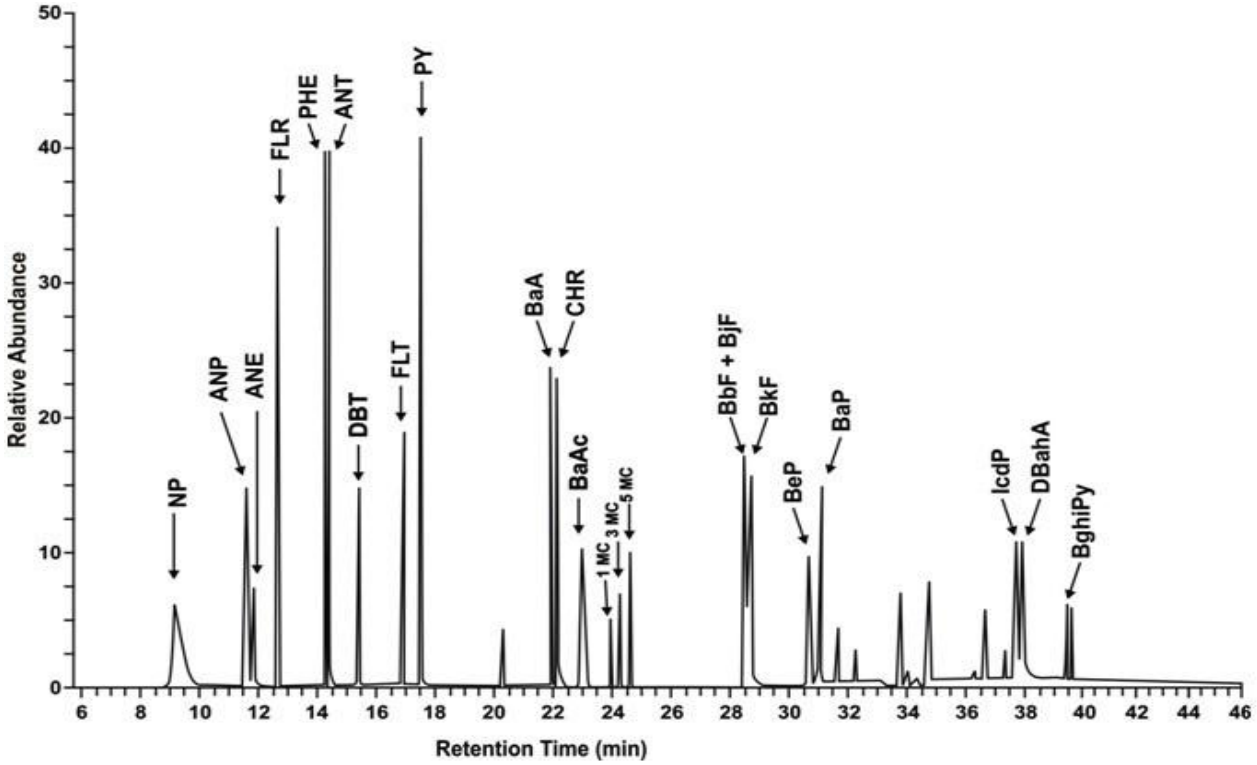

Figure-1 showing Chromatogram of the PAHs and Related Compounds Investigated at Badami Bagh

NP = Naphthalene, ANP = Acenephthylene, ANE = Acenaphthene, FLR = Flourene, PHE = Phenathrene, ANT = Anthracene, FLT = Fluoranthene, PY = Pyrene, BaA = Benzo(a)Anthracene, CHR = Chrysene, BbF = Benzo(b)Fluoranthene, BkF = Benzo(k)Fluoranthene, BaP = Benzo(a) Pyrene, IcdP = Indeno(1,2,3-c,d)Pyrene, DBahA = Dibenzo(a,h)Anthracene, BghiPY = Benzo(ghi)Perylene, DBT = Dibenzothiophene, BaAc = Benz(a)Acridine, 1MC = 1Methyl Chrysene, 3MC = 3Methyl Chrysene, 5MC = 5Methyl Chrysene, BeP = Benzo(e)Pyrene.
The statistically sum up data of PAHs is given in Table 1.

Table- 1. Concentration of PAHs at Badami Bagh

Sr. No.	Parameters	Min.	Max.	Mean
1	Naphthalene	6.9	29.7	18.45
2	Acenephthylene	11.7	21.6	14.4
3	Acenaphthene	0.0015	10.8	9.06
4	Phenathrene	14.1	163.5	49.5
5	Fluorine	5.4	159.6	20.1
6	Anthracene	4.2	24	14.1
7	Fluoranthene	9.3	128.4	22.35
8	Pyrene	3.3	57.6	30.45
9	Benzo(a)Anthracene	46.8	153.3	100.05
10	Chrysene	17.1	47.1	32.1
11	Benzo (b)Fluoranthene	1.5	188.7	95.1
12	Benzo (k) Fluoranthene	0.3	88.5	44.4
13	Benzo(a)Pyrene	0.6	143.1	71.85
14	Dibenzo(a,h) Anthracene	12.3	272.4	142.35
15	Indeno (1,2,3-c,d) Pyrene	0.003	36.9	18.45
16	Benzo (ghi) Perylene	18.6	108.9	63.75
	Total	**152.1045**	**1634.1**	**746.46**

The total concentrations of 16 PAHs varied from 152.1045 to 1634.1 **ngm^{-3}**, with a mean concentration of 746.46 **ngm^{-3}**. It was determined by Department of Health and Human Services (DHHS) that

benz[a]anthracene and benzo[a]pyrene were probably carcinogenic to humans. Numerous PAHs, including benz[a]anthracene, benzo[a] pyrene, benzo[b] fluoranthene, benzo [j] fluoranthene, benzo[k] fluoranthene, chrysene, dibenz [a,h] anthracene, and indeno [1,2,3-c,d] pyrene, were responsible for tumors in laboratory animals when they breathed these substances in the air (David, 1990). The industrial revolution and the rapid urbanization with increased usage of fossil fuels in public transportation, trucks, and the automobiles were the main reasons for increase in the levels of PAH in Agra. The countries with dry climate have exhaustive levels of PAH due to the high levels of particulate matter suspending in the atmosphere. According to a report, levels of PAH were found to be very high due to the arid climate and ranged between 130 and 190µg m^{-3} (Parmar *et al.*, 2001). In Agra, the characterization of atmospheric phase conditions with respect to the presence of inorganic constituents was done which included dry-deposition, fog, wet-deposition, and dew drops (Saxena, 1992; Saxena *et al.*, 1996; Kulshrestha *et al.*, 1995; Kumar *et al.*, 1996 and Parmar *et al.*, 2001). The mean values showing contribution in individual PAH compounds to total PAH's are given in Figure 2.

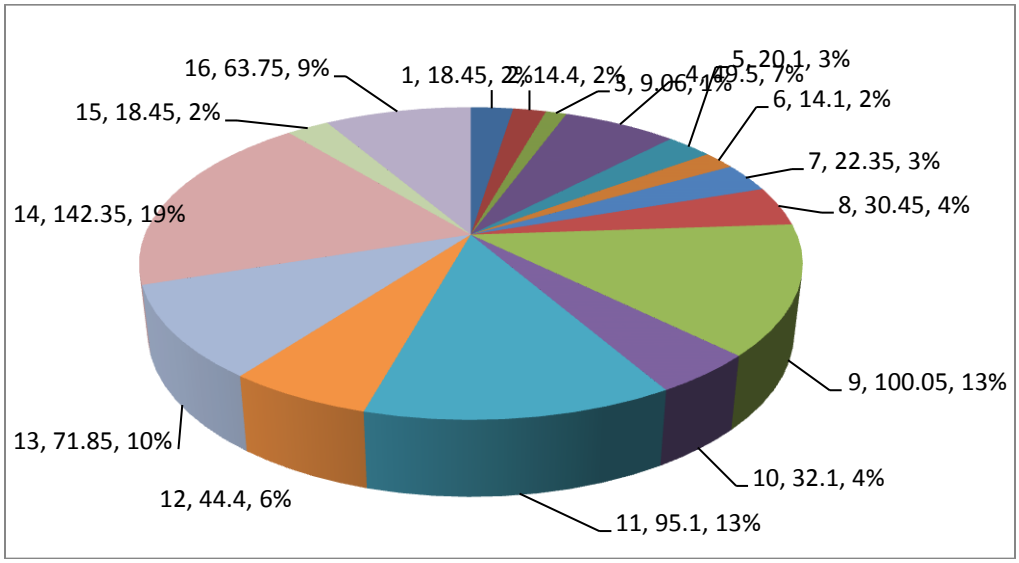

Figure-2 showing Mean values of PAH showing Contribution of the individual PAH compounds to the total PAHs

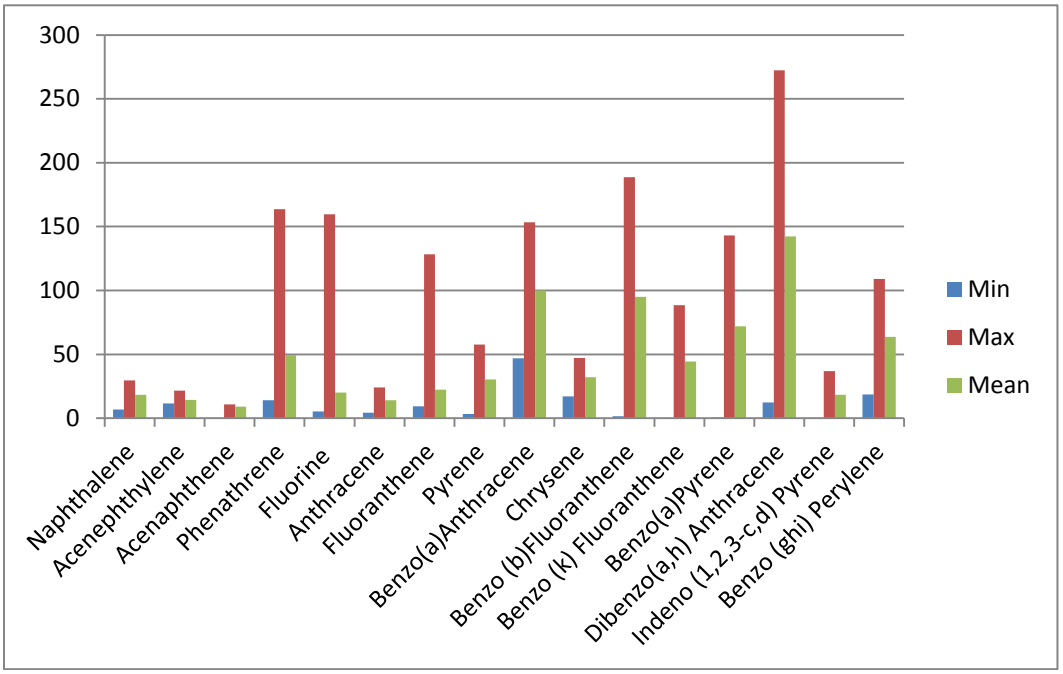

Figure-3 showing PAH's Minimum, Maximum and Mean Ranges

The concentration of PAH in urban areas may be tenfold higher than that of rural areas. All mentioned levels in the present study exceeded the WHO acceptable level i.e. 0.01ng m^{-3} (WHO Fact Sheet N313, 2014) Polycyclic aromatic hydrocarbons are considered as health hazards since many of them are carcinogenic and mutagenic giving way to acute and chronic health ailments (IARC, 1984; Menzie *et al*., 1992; Neilson *et al*., 1996 and Fang *et al*., 2004). Over the last few years, many countries with good industrialization have produced data regarding the airborne concentrations of polycyclic aromatic hydrocarbons such as 170 to 490ng m^{-3} in China (Simoneit *et al.*, 2001), 84.5ng m^{-3} in Brazil (Tavares *et al.*, 2004), 48.3 to 58.3ng m^{-3} in United States (Simick *et al.*, 1997), 20 to 164ng m^{-3} in United Kingdom (Coleman *et al.*, 1997 and Gardner *et al.*, 1995), 21.4 to 59ng m^{-3} in Urban Heraclion (Gogou *et al.*, 1996), and 7 to 9ng m^{-3} in urban Malaysia (Fang *et al*., 2004 and Omar *et al.*, 2002).

The present study was conducted to determine the concentration of polycyclic aromatic hydrocarbon in one of the busiest and heavy traffic areas named Yadgar Chowk, Lahore. The minimum, maximum and mean ranges of PAH are given in Figure 3. The average total concentration of PAH determined by Gas Chromatography was found to be 239 ngm^{-3}. Benzo (a) Anthracene (BaA) was found to be in highest concentration i.e. 58 ngm^{-3} among determined polycyclic aromatic hydrocarbons (Kalim *et al.*, 2015).

Conclusion: From the results it can be concluded that polycyclic aromatic hydrocarbons concentration is exceeding day by day in urban areas due to traffic load and various emission sources. In Badami Bagh area, the average total concentration of PAH was found to be 746.46 ngm^{-3}. Dibenzo(a,h) Anthracene was found to be in maximum concentration i.e. 142.35 ngm^{-3} and Acenaphthene was in minimum concentration of 9.06 ngm^{-3} among all the determined polycyclic aromatic hydrocarbons.

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