

Source apportionment of PM_{2.5} bound Polycyclic Aromatic Hydrocarbons from a Tricity in the foothills of Himalayas in Northern India

Sandeep Garg, Anita Rajor, Amit Dhir

Abstract— This study highlights variability in mass levels and source identification of PM_{2.5} bound polycyclic aromatic hydrocarbons (PAHs) in the tricity of Chandigarh, Mohali and Panchkula in India. The samples of PM_{2.5} were collected from industrial and residential and sensitive receptor sites during summer (April-May 2015) and winter (December 2015-January 2016) season. Sampling was done using medium volume sampler and chemical analysis was done using gas-chromatography technique. The average mass levels of PM_{2.5} varied from 31 to 91 $\mu\text{g m}^{-3}$ exceeding to NAAQ standard of 60 $\mu\text{g m}^{-3}$ and total PAHs varied from 5.76 to 75.62 ngm^{-3} with a seasonal variability as higher in winter than in summer season. The positive correlation between PM_{2.5} & TPAHs suggested similarity in source and origin. Diagnostic ratio and principal components analysis suggested vehicular emissions, coal combustion, wood and biomass burning as the main source of PAHs in the study area for potential health hazards.

Index Terms— Source identification, polycyclic aromatic hydrocarbons, Diagnostic ratio, Principal components analysis, Seasonal variability, Health hazards

I. INTRODUCTION

Airborne PAHs have been considered as major cause of adverse health impacts due to their carcinogenic (causing cancer) and mutagenic nature [1]. These are complex organic compounds which have at least two benzene rings in their structure having carbon – hydrogen bond between them [2]. They originate mainly from anthropogenic activities, such as incomplete combustion of coal, petroleum products, and biomass (pyrogenic sources) [3-4]. In the urban areas due to high vehicular density and low dispersion conditions, the mass concentration of atmospheric PAHs is generally very high [5]. Emissions from vehicular exhaust contain most of the PAHs classified as carcinogens [6].

United States Environmental Protection Agency has included a total of sixteen PAHs in the list of 188 Hazardous Air Pollutants [2].

The classification of PAHs can be performed on the basis of their molecular weights as less than or equal to four aromatic rings called as LMW and four or more aromatic rings as HMW PAHs [7]. PAHs of HMW are dominant over LMW. Various studies have showed LMW PAHs are considered as the products of wood, biomass and oil combustion [8-9] whereas HMW PAHs are associated with coal combustion and vehicular emissions [8], [10]. Therefore,

source identification can be done by using ratios between PAHs of LMW and HMW. Sources are considered for the ratio <1 as pyrolytic sources, while the ratios >1 as petrogenic sources [11]. Based on global atmospheric emission inventory of 16PAHs for the year 2004, India ranks 2nd with emissions of 90 Gg/year and also has higher proportion (3.6%) of hazardous high molecular weight (HMW) PAHs emissions than global average [12]. The PAHs show higher correlation with PM_{2.5} than PM₁₀ [13] and HMW fraction dominant over LMW [14].

As per literature, studies on airborne PAHs are reported through worldwide but limited to few cities of Delhi [15, 16], Mumbai [17], Ahmedabad [18] and Visakhapatnam [19] in India. No such study is evident in northern India particular to Chandigarh region. The present study focuses on the qualitative and quantitative data analysis and source identification of PM_{2.5} bound PAHs from a tricity of Chandigarh, Mohali and Panchkula region of Northern India.

II. MATERIAL AND METHODS

A. Sampling Site

The metropolitan region of Chandigarh Tricity includes Chandigarh-Mohali-Panchkula with over 2 million of population. Chandigarh is a union territory of India and serves as the combined capital of both states of Punjab and Haryana. Mohali and Panchkula are district head quarters of Punjab and Haryana states, respectively. Chandigarh is located in the foothills of Sivalik range of Himalayas and 162 miles (260 km) north of New Delhi, the national capital of India. The climate of Chandigarh is humid subtropical with varying temperature (–1 to 46 °C) and the annual average rainfall of 1110mm.

Ambient air samples for PM_{2.5} were collected at four sites, namely Sector 12 (Chandigarh), Sector 34 (Chandigarh), Sector 74 (Mohali) and Sector 12 A (Panchkula) (Fig.1). The location of Sector 12 (Chandigarh) is located in north-west of Chandigarh city in a green belt area. In the study area, NW is the prominent wind direction thus this station shall have least impacts from the anthropogenic and urban activities of this tricity. Furthermore, there is little habitation in this location with the presence of Shiwalik hills in the background. Sector 74 (Mohali) represents an industrial area comprising of various type of industries as engineering works, electrical/electronics, stationery, IT, pharmaceuticals and healthcare. Sector 34 (Chandigarh) represents a mix type of commercial cum residential areas in the downwind direction of city whereas Sector 12A (Panchkula) is purely a residential area. Among these three cities, Chandigarh city has the highest vehicle to population ratio.

Sandeep Garg, School of Energy and Environment, Thapar Institute of Engineering & Technology, Patiala-147004, India, +91-9814003103.

Dr. Anita Rajor, School of Energy and Environment, Thapar Institute of Engineering & Technology, Patiala-147004, India

Dr. Amit Dhir, School of Energy and Environment, Thapar Institute of Engineering & Technology, Patiala-147004, India

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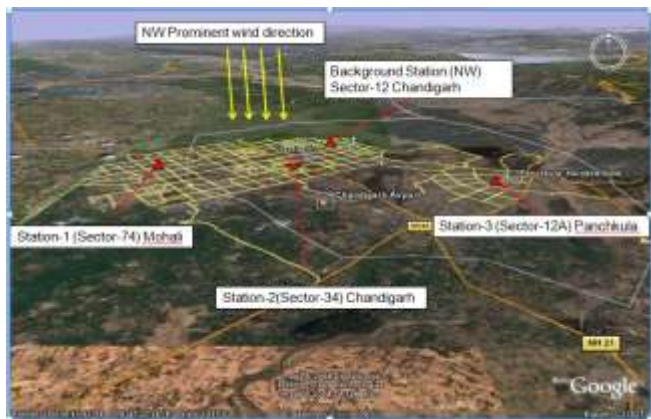


Figure 1: Location map of the study area

B. Sampling Procedure

The sampling was carried out as per CPCB guidelines (NAAQS) for 24h twice in a week over the summer season (April-May 2015) and winter season (December 2015-January 2016) for one year. The stations were located at suitable height >3m as per IS: 5182 (P-14) 2000. The laminar flow rate of the ambient air was 16.7 L/min (1m³/hr). Quartz filter paper having 47 mm diameter was used for sampling of PM_{2.5}. For removal of moisture content in the sample paper, it is mandatory to keep it in vacuum desiccators for 24 hour before and after the sampling. The monitoring and analysis was undertaken as per in NAAQS Monitoring and Analysis Guidelines Volume-1 (Guidelines for determination of PM_{2.5} in ambient air). A total of sixteen samples of PM_{2.5} were collected from each site using fine particulate sampler (Envirotech APM 550). After sampling to the extraction of PAHs, the filter papers were wrapped in aluminum foil and kept refrigerated (4°C) inside sealed plastic bags.

C. Analysis Procedure

A total of 64 samples of PM_{2.5} (sixteen from each location) were analyzed using standard method of IS: 5182 Part 12: 2004 (Methods for Measurement of Air Pollution-Polynuclear Aromatic Hydrocarbons in Air Particulate Matter). Each PM_{2.5} filter paper was extracted in 100ml toluene into a 200ml Erlenmeyer flask. The solution was ultrasonicated (Citizon Ultrasonic Processor) for 30 min at 20 Hz. The extract was filtered with the help of Whatman filter paper No. 41 (20) in the evaporated flask of 250 ml. The extraction was repeated twice and the extracts were combined. Rotary evaporator with temperature not exceeding 40°C was used for the evaporation of toluene extract until its volume was reduced to 1-2 ml. Added 2.0 ml of toluene to rinse the wall of evaporation flask and transfer the extract in to a beaker of 5 ml capacity. To clean up the impurities, silica gel column (length 200mm, and inner diameter 0.5 cm) was used. 3g slurry in cyclohexane of deactivated silica gel (60-120 mesh size) was taken and poured into the column. Toluene was eluted by cyclohexane through the column for conditioning. The sample extract was passed through the silica column and the resulting PAH fraction was collected within 5ml of cyclohexane. Finally 30ml of cyclohexane was added to the column to elute all organics of interest. The PAH fraction was collected in to the flask (reduced to about 1ml) and transferred in to 5ml capacity vials (stored in a dark and cool place).

The identification of PAHs was carried out using Gas Chromatography (Agilent) consisting of a capillary

column (DB-5), 25m x 0.2 mm inner diameter (ID) and flame ionization detectors (FID) in a split less mode. The injection and detector temperatures were 320°C. The carrier gas was N₂ @ 30ml/min. The calibration of GC was performed by known standard of Dr. Ehrenstorfer GmbH containing 14 analytes in acetonitrile. Three levels of concentrations were made from the original mixture. The peaks were identified on the basis of retention times and the amount of analyte was calculated.

HPLC grade solvents were used in the analysis. Total of sixteen PAHs were investigated, i.e., Acenaphthylene, Anthracene, Benzo(a) Anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(ghi)perylene, Benzo(K)fluoranthene, Chrysene, Dibenz(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-c,d) pyrene, Naphthalene, Perylene, Pyrene and Retene

D. Quality assurance in analysis

The accuracy for analysis was periodically checked using standard reference materials (SRMs). All sampled filter papers were stored at 4°C temperature after sampling. PAHs concentrations were calculated using retention times and peak areas of samples and standards. Blanks samples were also used for the accuracy of analysis. The detection limit of GC was determined using serial dilution of standard in a range of 0.008 to 0.020 ng/ml.

E. Principal components analysis using positive matrix factorization

PCA or PMF as a useful tool for source apportionment of PAHs was applied to multivariate data analysis [44], [47]. A number of data is reduced to small independent variables and each extracted factor corresponds to the specific source of PAHs. The factor loadings were carried out using SPSS after the varimax rotation to obtained correlation between factors and variables. Data with eigenvalue >1 for the factor were included in the matrix.

III. RESULTS AND DISCUSSION

A. Mass levels

As presented in figure 2, the mass levels of PM_{2.5} varied from 31 to 91 µg m⁻³ exceeding NAAQ standard of 60µg m⁻³. The results indicate PM_{2.5} as critical and serious concern which is affecting the air quality of this tricity.

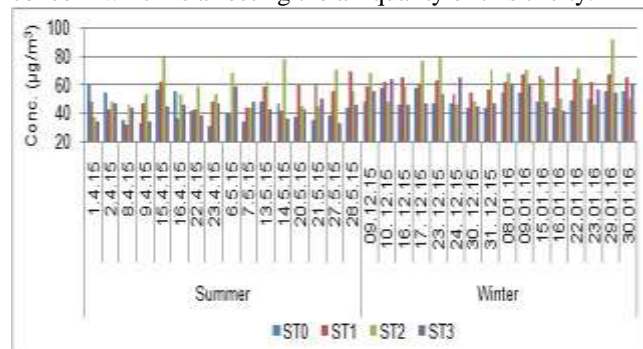


Figure 2: Mass levels of PM_{2.5} in the study area

A total of sixteen PAHs named Acenaphthylene, Anthracene, Benzo(a) Anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(ghi)perylene, Benzo(K)fluoranthene, Chrysene, Dibenz(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-c,d) pyrene,

Naphthalene, Perylene, Pyrene and Retene were determined in PM_{2.5} samples. A statistical summary of the individual PAH is presented Table I

Table I: Mass levels of polycyclic aromatic hydrocarbons (ng/m³) in the study area

PAH	Annual				Summer				Winter			
	Avg	Min	Max	SD	Avg	Min	Max	SD	Avg	Min	Max	SD
Acy	1.04	0.17	2.85	0.77	0.84	0.17	2.62	0.73	1.23	0.30	2.85	0.76
Ant	0.89	0.25	2.14	0.52	0.81	0.25	2.14	0.41	0.96	0.27	1.86	0.61
BaA	2.11	0.59	5.09	1.24	1.93	0.59	5.09	0.99	2.30	0.65	4.44	1.45
BaP	1.74	0.36	3.59	0.73	1.70	0.36	2.81	0.57	1.78	0.40	3.59	0.87
BbF	3.40	0.90	8.57	1.77	3.35	1.28	8.57	1.68	3.46	0.90	7.65	1.88
BghiP	2.25	0.32	7.95	1.69	1.81	0.32	4.36	1.57	2.70	1.17	7.95	1.70
BkF	2.62	0.55	6.08	1.24	2.31	0.55	4.84	1.34	2.93	1.65	6.08	1.06
Chry	4.41	0.65	15.78	3.58	4.25	0.65	13.30	3.42	4.56	0.68	15.78	3.77
dBahA	1.05	0.29	2.38	0.54	0.96	0.29	2.38	0.65	1.13	0.42	1.87	0.40
Fln	0.99	0.27	3.83	0.80	0.87	0.29	1.75	0.45	1.12	0.27	3.83	1.03
Flu	0.72	0.15	1.50	0.30	0.71	0.15	1.17	0.24	0.74	0.17	1.50	0.36
IP	1.66	0.34	2.98	0.64	1.57	0.34	2.98	0.85	1.74	1.20	2.38	0.29
Nap	1.62	0.43	4.08	0.84	1.56	0.90	3.49	0.64	1.68	0.43	4.08	1.01
Pery	1.57	0.26	6.55	1.51	1.49	0.42	6.55	1.55	1.65	0.26	4.35	1.48
Pyr	0.44	0.11	1.07	0.27	0.42	0.11	1.07	0.27	0.46	0.15	1.07	0.27
Ret	0.58	0.12	1.20	0.24	0.57	0.12	0.94	0.19	0.59	0.13	1.20	0.29
∑PAHs	27.09	5.76	75.62	16.68	25.16	6.78	64.06	15.55	29.03	9.06	70.47	17.21

The concentration of Total PAHs (∑PAHs) varied from 5.76 to 75.62 ngm⁻³ in the study area. Presence of LMW PAHs i.e. Flu and Ant indicates wood, grass and industrial oil combustion as a probable source [8], [19].

Table II: Comparison of mass levels and measurement techniques for polycyclic aromatic hydrocarbons [19].

Country	City	Extraction /Analysis	Mean/Range of TPAH (ng/m ³)	Samples collected	Site Description
India	Visakhapatnam	Acetonitrile-water/HPLC	57	PM ₁₀	Industrial/Residential
India	Agra	DCM /GC-FID	40 - 2500	SPM	Industrial
India	Delhi	DCM /GC-MS	33.1- 81.5	PM ₁₀	Roadside/ Residential
India	Tiruchirapalli	DCM: methanol/HPLC	232.7	PM _{2.5}	Residential
Hong kong	Kwun Tong	DCM / GC-FID	2- 269	PM ₁₀	Industrial/Residential
Taiwan	Taichung	DCM /GC-MS	180.62	PM _{2.5}	Residential
Greece	Elefsina	Acetonitrile/HPLC	0.6- 38.3	PM ₁₀	Industrial
Turkey	Zonguldak province	Hexane -acetone/HPLC	28	PM ₁₀	Industrial
Present Study	Chanidigarh-Mohali-Panchkula	DCM / GC-FID	5.76 - 75.62	PM _{2.5}	Industrial, residential & Educational

The presence of HMW PAHs i.e. Fln, Pyr, Chry, BaA, BbF, BkF, BghiP, BaP, Pery, dBahA, and IP is mainly due to vehicular emissions [8], [10], industrial sources [20] and coal combustion [2], [8], [21], [22].

B. Seasonal Variations

Particulate aerosols show a significant seasonal variability mainly associated to meteorological conditions, type and strength of source and atmospheric chemistry [23-27]. As illustrated in Figures, the mass concentration of PM_{2.5} and its associated PAHs are observed as higher in winter than summer [28-29]. The higher concentrations in winter may associated to increased coal and bio fuels burning plus higher exhaust emissions from automobiles and engine sets due to cold start [30-31]. Stagnant atmosphere and calm conditions in winters are conducive for the

formation of particulate aerosols [32-33]. Crop stubble burning in October-November after rice harvesting and in March-April after wheat harvesting could be another reason [34].

C. Diagnostic Ratios

PAHs and other semi volatile organic compounds were used as tracers to identify diverse sources. Diagnostic ratios of PAHs can be used to categorize anthropogenic and biogenic sources of emission. Despite from these facts, ratios act as a fingerprint of emission sources and can be used to differentiate between various PAHs and their potency of having carcinogenic and mutagenic effects. The emission sources can determine by comparing the values of present study with the values given by various authors, who

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established possible ranges indicating the source of emission of various PAHs [19], [35], [36].

In this study, the diagnostic ratios were calculated for IP/(IP+BghiP), BaA/(BaA+Chy), BaA/BaP, BbF/BkF are presented in Table III. The ratio of IP/(IP+BghiP) as 0.42 under the range 0.37-0.70 and the ratio of BbF/BkF in the range 1.29-1.31 suggests the influence of diesel emissions

[19], [37], [38]. The ratio of BaA/BaP as 1.21 indicates biomass burning [39] and the ratio of BaA/(BaA+Chy) as 0.32 (0.20-0.35) indicates coal combustion [40] in the study area. The diagnostic ratios performed in the study highlight the influence of multiple sources as vehicular emissions, coal and Biomass burning as the main source of PAHs in the study area.

Table III: Diagnostic ratio with source, range and reference studies

Diagnostic Ratios	Present Study	Range	Sources	Conclusion	References
IP/(IP+BghiP)	0.42	0.18-0.20	Gasoline	Oil Combustion	[19]
		0.37-0.70	Diesel		[37]
		0.56	Coal		
		0.62	Wood		
BaA/BaP	1.21	0.90-1.70	Diesel	Wood Combustion	[39]
		0.5-0.70	Gasoline		
		1.0-1.5	Wood		
BaA/(BaA+Chy)	0.32	0.38-0.64	Diesel	Coal Combustion	[40]
		0.20-0.35	Coal		
BbF/BkF	1.29	>0.5	Diesel	Diesel Combustion	[19],[38]

D. Principal component analysis (PCA)

PCA with varimax rotation was applied to determine the sources of PAHs in the study area of a tri-city.

Table IV: Source identification and factor analysis using PCA technique

PAH	Factor 1	Factor 2	Factor 3
Acy	.941	-.070	-.223
Ant	-.042	.919	-.199
BaA	-.042	.919	-.199
BaP	.392	.258	.874
BbF	.207	.606	-.078
BghiP	.936	.106	-.099
BkF	.958	.003	-.131
Chry	.402	.477	.403
dBahA	.929	-.113	-.157
Fln	.862	.098	-.132
Flu	.393	.256	.875
IP	.854	-.055	-.024
Nap	.135	.900	-.183
Pery	.827	-.200	-.332
Pyr	.962	-.088	-.189
Ret	.390	.259	.875
Eigenvalue	7.31	3.38	2.84
Variance (%)	45.70	21.14	17.76
Cumulative (%)	45.70	66.84	84.60
Source	Vehicular Emission	Coal Combustion	Wood & Biomass Burning

The first factor represents high loading of Acy, Ant, BghiP, BkF, dBahA, Fln, IP, Pery and Pyr with a total variance of 45.70%. Various studies have reported BghiP, BkF, dBahA and IP in vehicular emissions [2], [19], [41], [42] as BkF is the marker for diesel emissions [8], [43] whereas the Acy Pery and IP are the tracers of gasoline emissions [2], [29].

The second factor represents a total variance of 21.14%. The high loading of Ant, BaA, BbF, Chry and Nap indicates coal combustion as the source [19], [44], [45].

The third factor represents a total variance of 17.76%. The high loading of BaP, Flu and Ret indicates biomass and wood burning as the source [8], [19], [44], [45]. Various researchers have indicated the marker of biomass and or wood burning as Ret [46] BaP and Flu [41].

E. Evaluation of health risks

Among the PAHs studied, BaP is considered as the most powerful tool as reference chemical/ indicator for estimating the risk level imposed by all PAHs because of their well characterized toxicity. A toxic equivalency factor (TEF) also called as relative potency factor (RPF) was taken for each compound by multiplying the concentration of each compound with its corresponding TEF value given in table below and then summing up the results for BaP equivalent (BaP_{eq}). TEF or RPF from the EPA were taken into account as reference values in present study.

The mathematical expression for calculation of BaP equivalent (BaP_{eq}) is defined as $\sum \text{Conc}_n * \text{TEF}_n$

Where,

Conc._n= Concentration of Individual PAH

TEF_n= Toxic Equivalency factor

Table V: PAHs and their toxic equivalency factor

S. No.	PAH Compound	TEF- Toxic Equivalency factor
1	Acenaphthylene (Acy)	-----
2	Anthracene(Ant)	-----
3	Benzo(a)pyrene (BaP)	1
4	Benzo(a)anthracene (BaA)	0.1
5	Benzo(b)fluoranthene (BbF)	0.1
6	Benzo(k)fluoranthene (BkF)	0.01
7	Benzo(g,h,i)perylene (BghiP)	0.01
8	Chrysene (Chy)	0.001
9	Dibenzo(a,h)anthracene (dBahA)	0.1
10	Fluoranthene (Fln)	0.001
11	Fluorene (Flu)	-----
12	Indeno(1,2,3)pyrene (IP)	0.1
13	Napthalene (Nap)	-----
14	Pyrene (Pyr)	0.001
15	Perylene (Pery)	-----
16	Retene (Ret)	-----

In present study, the total Bap_{eq} concentration reported as 2.61 ng/m³ was higher than BaP standard of 1 ng/m³. The result indicates that PAHs can impose adverse impacts on human health in the study area.

IV. Conclusion

In present study, the average mass levels of PM_{2.5} varied from 31 to 91 µg m⁻³ exceeding NAAQ standard of 60µg m⁻³ indicating alarming situation of air quality in the region. The average concentration of TPAHs varied from 5.76 to 75.62 ngm⁻³ during entire study period. The mass levels of PM_{2.5} and total PAHs show seasonal variability as higher in winter than in summer season. The positive correlation between PM_{2.5} & total PAHs suggested similarity in source and origin. PCA suggested vehicular emissions, coal combustion, wood and biomass burning as the main source of PAHs in the study area.

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