

Source Apportionment of PM_{2.5} Bound PAHs in Tropical Tiruchirappalli City, India

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The aim of this study is to investigate the distribution and sources of polycyclic aromatic hydrocarbons (PAHs) as per the priority list of USEPA, bound to fine particulate matter (PM_{2.5}) prevalent in Tiruchirappalli, an urban city of India. The sampling was carried out for 24 h continuously in each station to study the PM_{2.5} deposition. The PAHs deposited on the filter paper was estimated using ultrasonic centrifuge solid-phase extraction method and further analyzed with gas chromatography mass spectroscopy (GC-MS). The results showed that the range of PAHs concentrations in the study period was between 1.0 and 90.20 ng/m³. The seasonal variation of all the 16 PAHs varied from 38.78 ng/m³ in monsoon, 32.06 ng/m³ in winter, 12.54 ng/m³ in summer and 8.88 ng/m³ pre-monsoon. The annual average concentration of PAHs observed was 22.51 ng/m³ with PAHs of higher molecular weight in abundance accounting for almost 90.81 % while the PAHs of lower molecular weight contributing to 9.23 %. Higher PAHs levels of 35.41 ng/m³ were recorded during cold months followed by 10.71 ng/m³ during warm months. Diagnostic ratio source analysis and principal component analysis established that vehicular emissions and off-road combustion sources were the major sources. The mean benzo(a)pyrene toxicity equivalent calculated for samples was 2.83 ng/m³ and the mean contribution of the carcinogenic potency of benzo(a)pyrene was observed to be 41.13 %.

Keywords: Urban air quality, Fine particulate matter, Polycyclic aromatic hydrocarbons, Health risk, Toxicity.

INTRODUCTION

The current scenario in industrial and technological development has triggered the rapid decline of environmental quality throughout the world. Among the environmental deodorization, air pollution is a serious global issue and especially the urban cities are drastically becoming inferior. Particularly, the particulate matter is a major concern throughout the world in both, developed and developing countries [1]. The predominant causes of air pollution are directly proportional to the intermittent increase of human population and vehicular emission. The particulate matter can be released directly into the atmosphere or synthesized secondarily from precursor gases as a result of physical and chemical transformations [2]. Among the particulate matters, fine particulate matter (PM_{2.5}) is implicated in numerous human health issues throughout the world [3]. Also, the PM_{2.5} contains broad range of toxic compounds

that can be inhaled and cause serious health problems owing to its chemical composition [4]. Especially, PAHs are one of the important toxic components associated with PM_{2.5}. Liu *et al.* [2] reported that more than 80 % of PAH particles were associated with PM_{2.5} and PAHs concentrations in particulate matter are highly dependent on these fine particles which can reach the alveolar region of the respiratory system increasing their potential health effects. Polycyclic aromatic hydrocarbons (PAHs) are comprised of carbon and hydrogen atoms which are dangerous for human health with well established mutagenic and carcinogenic properties. Apart from, human activities that contribute the most to PAHs emissions and incidentally the vehicular emission is often reported as one of the most vital sources and these sources are entirely anthropogenic in urban and industrial atmospheres [1,5,6]. Many studies have investigated in ambient PAH levels, sources in different cities around the world [1,7,8] and it is inferred that the concentration

depends largely on the area while the urban cities and industrial area are the most affected zones.

Due to the rapid urbanization, mushrooming of industrialization have been triggered the growth of transportation. Consequently, many Indian cities suffer from severe air quality defects. Unfortunately understanding the chemical composition and the health hazards of particulate matter still remains a challenge in many urban cities. Thus, for evaluating such impacts, a fact-finding survey was vital. In this study, attempts were instituted to know the level of air contamination in Tiruchirappalli city of India. The main objective of the study was to validate the quality of respirable fraction of particulate matter associate polycyclic aromatic hydrocarbons (PAHs) sources in a typical urban site of Tiruchirappalli city, India.

EXPERIMENTAL

Study area: Tiruchirappalli city (10.5°N, 78.43°E, 78.8 MSL), is situated on the banks of river Cauvery, India. Total geographical area of the city is 164.70 km² with the total population of one million as per 2011 census within its municipal corporation. In 2017, the total population had increased to 1.2 millions and the number of vehicles registered with the Regional Transport Authority exceeding 0.7 million in the municipal area. Four major highways NH-45, NH-67, NH-210 and NH-277 pass through the city. The heavy traffic on these highways have significantly altered the air quality in the city [9,10]. Sampling was conducted at five sampling sites, located in distinctly different over the Tiruchirappalli city and Fig. 1 shows the location of all the sampling sites. The sampling locations were selected at Jamal Mohamed College-TVS Tollgate (JMC), Orchard School-K.K. Nagar (OrdS), Central bus Stand (CeBS), Thillai Nagar (ThN) and Chathiram bus stand (ChBS). The station JMC (10°47'11.72"N, 78°41'40.85"E) is surrounded by educational, residential buildings and national highway (NH-45). At OrdS station, samples were collected from the Orchard school building (10°45'34.70"N 78°40'52.02"E) and this station was located at the center of residential area. Also OrdS lies on the outer border of Tiruchirappalli city. At CeBS station, samples were collected on Shri Sangeetha tower which is located near the central bus stand (10°47'57.63"N, 78°41'1.22"E). It is surrounded by scattered inhabited residences and heavy traffic. The ThN station samples were collected from Cethar hospital in Thillai Nagar (10°49'26.43"N, 78°41'3.89"E). This site is surrounded by high-rise residential buildings, many hospitals and traffic. Similarly at ChBS station, samples were collected at hotel Chitra of Chathiram bus stand (10°50'0.65"N, 78°41'34.96"E). This site is encamped by busy traffic, commercial sites being the city's second largest bus stand. The samplers were placed on the rooftop of buildings in all sampling sites, at an altitude of 15 m from the ground level.

Samples collection: Two PM_{2.5} samplers (TH100-PM2.5 cascade impactor, Wuhan Tianhong Instruments, Wuhan, China) were placed at each site in parallel. The samples were collected during June 2015 to July 2016, January-February, March-May, June-September and October-December were defined as winter, summer, monsoon and post-monsoon, respectively. Detailed weather scenario during these sampling days are tabulated in Table-1. Samples were collected for 24 h continuously in each

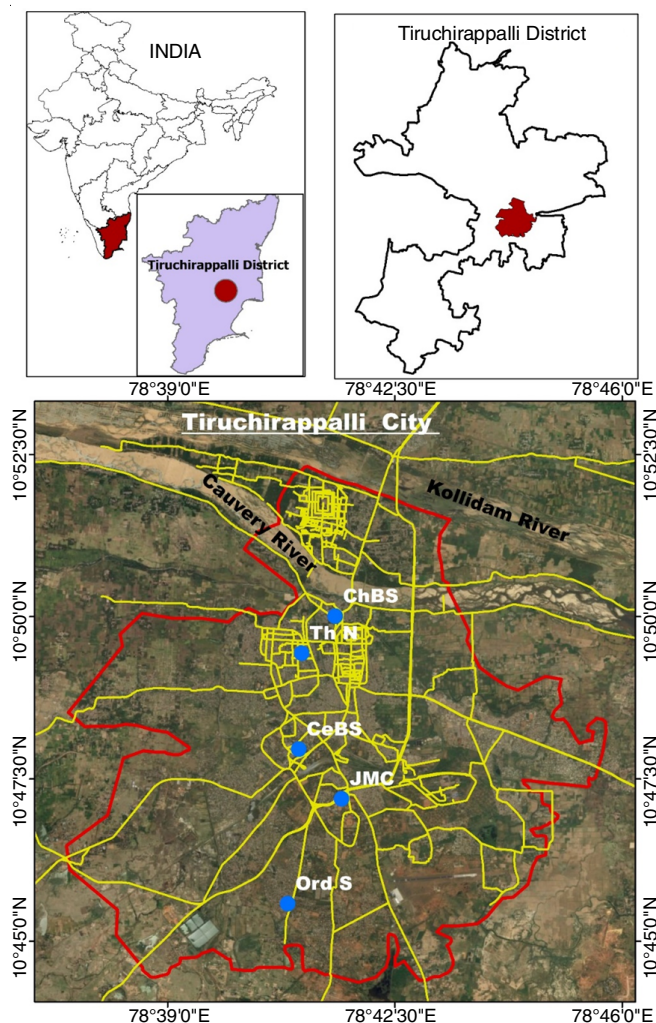


Fig. 1. Location of the sampling site at Tiruchirappalli, India

station and the flow rate was maintained at 100 ± 2 L min⁻¹. In this study, quartz filters-Whatmann, QM-A quartz filters 90 mm (Quartz microfiber filters: Whatman, GE Healthcare Life Sciences, UK) were used for the analyses. To remove all impurities all blank quartz micro filters were conditioned at 600 °C for ~8 h in a muffle furnace and then stored in a refrigerator at 4 °C for consequent analysis.

Chemical analysis and quality control: USEPA TO-13A, method 3550B with ultrasonic extraction and silica gel cleanup was used to quantify the PAHs collected in quartz micro filters. Surrogate PAH solution containing naphthalene d8 (Nap-d8), acenaphthene-d10 (Acp-d10), phenanthrene-d10 (Phe-d10), chrysene-d12 (Chr-d12) and perylene-d12 (Pery-d12) was spiked directly to the quartz microfiber filters to compare and contrast recovery rates before it is soaked in DCM for a duration of 10 h and extracted thrice ultrasonically. The extracts were concentrated to 10 mL, using rotary evaporator, after adding 15 mL of *n*-hexane, the extract was condensed to around 1 mL for solvent exchange and then purified on a silica gel column. Next 10 µL of 10 µg/mL hexamethyl benzene solution was added to the tube and the supernatant was transferred to a vial insert for GC/MS analysis. Sixteen PAHs were analyzed using an Agilent 6890 GC coupled with an Agilent 5973 MSD operated in selective ion monitoring mode. A 30 m × 0.25 µm HP5-MS capillary column

TABLE-1
AVERAGE CONCENTRATION OF PAHs ASSOCIATED WITH PARTICULATE MATTER PM_{2.5} TIRUCHIRAPPALLI CITY, INDIA, DURING FOUR SEASONS (JULY 2015-JULY 2016) (n = 108). MEAN PAH CONCENTRATIONS (ng/m³)

Sampling sites	Nap	Acpy	Acp	Flu	Phe	Ant	Flua	Pyr	BaA	Chr	BbkF	BeP	BaP	IP	BghiP	DBA	TPAHs
Winter																	
JMC	0.19	0.1	0.09	0.1	0.77	0.2	1.35	2.08	1.5	2.48	2.44	2.44	3.33	2.24	2.52	0.75	22.59
OrdS	0.23	0.13	0.1	0.12	0.83	0.24	2.03	4.23	1.48	2.03	2.03	0.22	3.18	3.25	2.94	2.03	25.06
ThN	0.19	0.16	0.13	0.17	1.04	0.25	1.78	4.46	1.48	1.91	2.6	2.77	3.91	3.65	3.58	1.5	29.57
CeBS	1.53	0.39	0.67	0.27	1.29	0.4	2.23	4.22	3.11	3.87	5.19	5.08	7	7.05	7.29	1.93	51.51
ChBS	0.19	0.09	0.09	0.14	0.75	0.24	1.54	2.82	1.49	2.1	2.6	2.78	3.34	3.77	4.31	1.25	27.51
Summer																	
JMC	0.66	0.19	0.19	0.19	0.84	0.27	0.92	2.14	1.1	1.26	0.79	0.8	1.44	0.85	1	0.23	12.87
OrdS	0.61	0.25	0.15	0.2	0.77	0.31	0.61	2.02	0.37	0.5	0.59	0.71	1.07	1.91	2.19	2.17	14.42
ThN	0.04	0.04	0.11	0.09	0.34	0.13	0.41	1.58	0.33	0.43	0.64	0.64	0.76	0.78	1.05	0.29	7.68
CeBS	0.35	0.3	0.22	0.22	0.94	0.35	1.04	4.97	0.4	0.46	0.46	0.48	0.91	0.59	0.7	0.24	12.64
ChBS	0.27	0.1	0.15	0.11	0.44	0.18	0.37	1.54	0.04	0.08	0.04	0.04	0.11	0.04	0.03	0.09	3.64
Southwest monsoon																	
JMC	0.76	0.15	0.05	0.18	0.94	0.13	0.7	1.14	0.68	2.44	1.8	1.74	1.67	0.47	1.13	0.1	14.1
OrdS	0.22	0.12	0.11	0.15	0.53	0.21	0.56	2.27	0.32	0.43	0.48	0.58	1.02	0.95	1.26	0.6	9.8
ThN	0.58	0.16	0.05	0.1	0.53	0.1	0.34	0.65	0.17	0.44	0.44	0.49	0.57	0.73	0.97	0.24	6.55
CeBS	0.75	0.18	0.03	0.08	0.55	0.07	0.46	0.56	0.24	1.22	1.19	1.19	0.63	0.33	0.89	0.06	8.46
ChBS	0.68	0.28	0.05	0.12	0.77	0.12	0.54	0.8	0.24	0.88	0.48	0.51	0.29	0.18	0.48	0.05	6.47
Northeast monsoon																	
JMC	0.52	0.28	0.1	0.21	1.2	0.27	2.08	3.76	2.64	3.4	3.25	3.27	5.78	3.57	3.75	1.11	35.19
OrdS	0.31	0.1	0.06	0.1	0.6	0.15	0.77	1.3	0.66	1	1.8	2.08	2.31	3.7	3.26	1.1	19.29
ThN	0.19	0.08	0.06	0.11	0.6	0.18	1.09	2.19	1.05	1.47	1.93	2.09	3.24	3.52	3.57	1.09	22.45
CeBS	0.75	0.23	0.21	0.18	1.13	0.3	1.84	3.08	2.51	3.95	4.54	4.81	6.32	5.72	7.35	1.64	44.55
ChBS	0.66	0.23	0.08	0.19	1.3	0.33	2.4	4.77	3.04	4.68	5.97	6.24	7.69	7.59	8.49	2.08	55.73

was used to separate these compounds with an oven temperature program from 60 to 300 °C.

The recovery range of surrogate PAHs ranged from 86 to 92 %. Blank samples were analyzed to study the existence of field and laboratory contaminations if any. Two pairs of duplicate samples too were treated with samples under study and the difference between the two was less than 9.2%. The recovery rates and blank values were corrected with reported concentrations of PAHs. Each compound was compared to the amount added to calculate the recoveries. The mean recovery yield of 18 PAHs ranged between 70.2 % and 91.0 %. Eighteen PAHs viz. naphthalene (Nap), acenaphthylene (Acpy), acenaphthene (Acp), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benz(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(j)fluoranthene (BjF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno(1,2,3-cd)pyrene (IP), dibenz(a,h)anthracene (DBA) and benzo(ghi)perylene (BgP), were analyzed using an Agilent 6890 GC coupled with an Agilent 5973 MSD operated in selective ion monitoring mode.

RESULTS AND DISCUSSION

Concentrations of PAHs: In the present study, particulate PAHs concentrations were measured at five sites situated in Tiruchirappalli city, India, an urban tropical background. Annual average concentrations of 16 PAHs observed in five sampling stations, i.e., CeBS, ChBS, JMC, OrdS and ThN were of 32.06, 26.35, 23.15, 17.45 and 15.18 ng/m³, respectively (Table-1). The maximum total PAH level of 32.06 ng/m³ was recorded at Central bus stand (CeBS) followed by Chathiram bus stand (ChBS) 26.35, 23.15 ng/m³ and Jamal Mohamed College (JMC) 17.45 ng/m³.

Central bus stand (CeBS) is the busiest station of Tiruchirappalli city with high traffic round the clock with the Railway Junction nearby. A radius of almost 1 Km around the site is surrounded by restaurants of different caliber ranging from high class to roadside cafeteria mostly dependent of wood as fuel. Chathiram bus stand (ChBS) is also one of the main hubs in Tiruchirappalli being the busiest bus station with high vehicular traffic throughout the day too was the major emission source. Moreover, presence of large number of hotels in the neighborhood and their kitchen emissions were also likely to contribute to ambient PAH. In JMC site, is at the cross section of National highways experiences emissions from traffic and automobile service station, Orchard School (OrdS) and 15.18 ng/m³ Thillai nagar (ThN). Thillai nagar (ThN) site is surrounded by most of the multi-specialty hospitals of the city and major commercial activities, intermittent emissions from vehicular traffic. Orchard school (OrdS) sampling site can be considered as a suburban area surrounded by numerous residential sites and villages. The Orchard school site is situated at the cross road leading to the airport which attracts vehicular emissions from continuous traffic. Roadside hotels and houses in villages in the suburbs still burn solid wood as fuel which could be a source of PAH emission. Open garbage burning also might have contributed to the ambient PAHs in all sites.

The annual average atmospheric concentration of all the 16 PAHs determined in PM_{2.5} at Tiruchirappalli city was 23.94 ng/m³ and ranged from 1.00 µg/m³ to 90.53 ng/m³. The most abundant PAHs were those with higher molecular weight, accounting for 90.81 % and lower molecular weight PAHs and accounting for 9.23 %. It is inferred that higher molecular weight PAHs with the lowest vapor pressure are a group of compounds

with the tendency to be strongly associated with particle phase than that with lower molecular weight [11] and hence deduced that the ability of the particles to carry PAHs depends on their molecular weight and vapor pressure. PAHs exhibiting high molecular weight and low vapor pressure are susceptible to increased absorption rate in the particle phase [11]. This observation suggests that combustion of gasoline is one of the major sources of PAHs compounds in the area of the study, which is consistent with results of Zielinska *et al.* [12].

Table-2 shows the comparisons of mean and range of PAH concentration in this study with other major cities across the world. The total average PAH concentrations (22.48 ng/m³ Σ 16 PAHs) in PM_{2.5} were close to Cuernavaca (24.0 ng/m³, Σ 15 PAHs) was similar to that reported in Taichung, China (22.29 ng/m³, Σ 15 PAHs) [13], and Beijing, China (28.5 ng/m³ Σ 16 PAHs [14]. It was lower than that reported for Nanjing (62.58 ng/m³, Σ 15 PAHs) [15], Tehran, Iran (44.2 ng/m³ Σ 16 PAHs) [16], Shenzhen, South China. 128 ng/m³ Σ 16 PAHs [14]; Agra, India (42.3 ng/m³ Σ 18 PAHs) [17], Seoul, South Korea (89.3 ng/m³ Σ 15 PAHs) [18], Chennai, India (5517 ng/m³ Σ 11 PAHs) [19], Coimbatore, India 90.4 ng/m³ Σ 13 PAHs [20]. All these places have the characteristic of being large urban areas with high vehicular activities.

Study area	Number of PAHs	Σ PAHs (ng/m ³)	Mean level (ng/m ³)	Ref.
Beijing, China	16	5.9-362.1	28.5	[14]
Tehran, Iran	16	2.1-410.3	44.2	[16]
Shenzhen, South China	16	110-190	128	[14]
Agra, India	18	8-97.9	42.3	[17]
Seoul, South Korea	15	11-350	89.3	[18]
Chennai, India	11	121.1-1,370	5-517.1	[19]
Coimbatore, India	13	20-172	90.4	[20]
Tiruchirappalli, India	16	1.0-90.53	22.51	Present study

Spatial and seasonal patterns: Seasonal means analysis of the total PAHs concentrations in the study area revealed comparatively higher values during northeast monsoon and winter seasons, southwest monsoon and summer seasons, respectively. The annual average PAHs mass concentrations in PM_{2.5} in northeast monsoon, winter, summer and southwest monsoon were 38.61, 35.74, 12.54 and 8.88 ng/m³, respectively (Fig. 2). Similarly, higher PAHs levels were recorded during cold months 35.41 ng/m³ followed by warm months 10.71 ng/m³. It is also substantiated with previous findings that the concentration was 10-15 folds higher in winter than summer [21,22]. The increase in particulate total PAH concentration during the winter and the dependence of PAH concentration on atmospheric temperature have been reported in several places [23-25]. Source emissions and meteorological conditions as well as gas particle partitioning may result in winter and summer difference of PAHs concentrations [26]. Reduced atmospheric dispersion resulting from lower mixing height as well as reduced

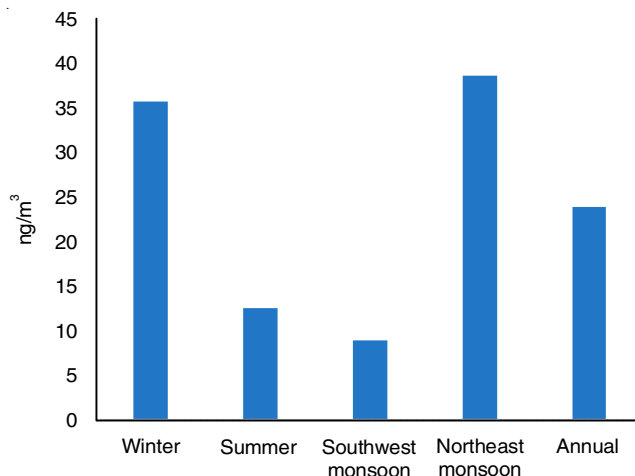


Fig. 2. Total PAH concentrations of PM_{2.5} in winter, summer, southwest monsoon and northeast monsoon

atmospheric reaction can lead to higher pollutant concentration in ambient air during cold months.

The overall seasonal analysis of the present study suggest that PAHs of higher molecular weight show higher concentrations during northeast monsoon and winter. It also portrays that it is influenced by urban structures and micro-climatic conditions apart from lower temperature, weaker radiation strength, additional emission sources during cold months [27,28]. Mixing height of pollutants also decrease with fall in temperature [29]. The probable mechanism for this phenomenon is that the low molecular weight PAHs in the particle phase easily transits in to vapour phase forming higher mixing layer at higher temperatures and *vice-versa*. The mean temperature in cold months is approximately lower than that in warm months and the PAHs concentrations in cold months is 3.31 times higher than that in warm months. This indicate that PAHs are photochemical degraded easily in warm months.

Evaluation of health risk: PAHs are widely distributed and persistent in nature, are the world's first and the largest class of carcinogen with the ability to cause gene mutation and cancer. These PAHs that enter the atmosphere travel long distances before they get adsorbed onto the soil, vegetation and water bodies becoming recalcitrant in the environment, through precipitation [29-31].

Benzo[*a*]pyrene (BaP) is considered as the most powerful mutagens acts as a PAHs indicator and is regarded by WHO as a good index for PAH carcinogenicity. In present study, the average concentration of BaP in five sampling sites varied between 1.43 and 4.22 ng/m³, exceeding the NAAQS 2009 annual average of 1 ng/m³. The BaP degrades easily in the presence of sunlight and other oxidants. The BaP concentrations alone does not act as an indication of hazards pertaining to PAHs and its carcinogenic character under predetermine conditions if only the compound is takes as the representative of carcinogenicity. Therefore, an equivalent index for BaP (BaPE) was created with the objective of allowing a better estimation of carcinogenic potential associates with atmospheric particle. The concentration of BaPE for each PAH was calculated by multiplying their concentration by its corresponding toxic equivalent factor (TEF), which represents the relative carcinogenic potency of the corresponding PAH [32-34]:

$$\text{BaPE} = \text{BaA} \times 0.06 + \text{BF} \times 0.07 + \text{BaP} + \text{DBaH} \times 0.6 + \text{IP} \times 0.08$$

where BF includes all the isomers of benzofluoranthene. The BaPE index tries to parameterize the health risk for human health related to ambient PAH exposure and was calculated by multiplying the concentrations of each carcinogenic congener with its carcinogenic factor obtained by laboratory studies.

The annual average value obtained for BaPE in this study was 2.83 ng/m³ and the current sampling site wise TEF values are 3.70 in CeBS, 2.98 in ChBS, 2.78 in JMC, 2.59 in OrdS and 1.79 in ThN, respectively. This values are lower than that reported for Zonguldak, Turkey (14.1 ng/m³ and Nanning, China (7.1 ng/m³). However, it was higher than that found in Florence, Italy (0.92 ng/m³) and Hamilton, Canada (0.84 ng/m³). The compounds used to calculate BaPE (BaA, BaP, BbF, BkF, IP, DBaH) represent 41.20 % of PAHs identified in Tiruchirappalli city, which constitutes a risk factor for the exposed population, taking into account the high degree of penetration in the respiratory system that have the PM_{2.5} particles. The average total BaPeq concentrations of the 16 PAHs in the PM_{2.5} for winter, summer, southwest monsoon and northeast monsoon were 4.80, 1.57, 0.74, and 4.95 ng/m³, respectively. The total BaPeq concentrations of PM_{2.5} exhibited significant seasonal variations (ANOVA *p* < 0.05). The total BaPeq concentrations during the four seasons were in the order northeast monsoon > winter > summer > southwest monsoon (Fig.3). Higher BaPeq concentrations of PM_{2.5} were recorded during cold months 4.88 ng/m³ followed by warm months 1.15 ng/m³. This study indicating that people with exposure to PM_{2.5} bound PAHs are at an increased risk of carcinogenic exposure in cold winters than in hot summers.

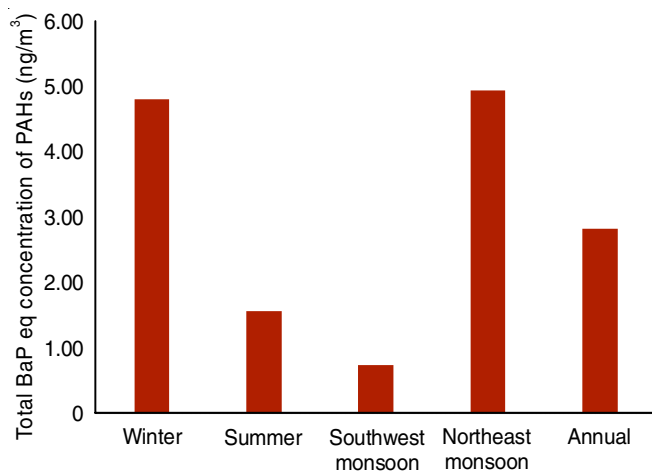


Fig. 3. Total BaPeq concentrations of PAHs in PM_{2.5} in winter, summer, southwest monsoon and northeast monsoon

Source analysis

Diagnostic ratios: The diagnostic ratios are used to characterize and identify major PAH source in different environmental media [33]. These ratios help distinguish PAH emission from various sources such as solid fuels, liquid fuels and biomass combustion. The ratio (Flt/(Flt+Pyr)) below 0.4 implies the prominence of unburnt petroleum products, ratios from 0.4 to 0.5 suggests the combustion of liquid fossil fuels, whereas ratios larger than 0.5 are characterized for grass, wood or coal combustion. In this study, the ratios below 0.4 implies the prominence of unburnt petrogenic sources.

In this study, the Flt/(Flt+Pyr) ratios below 0.40 (range from 0.26 to 0.36) implies the prominence of unburnt petroleum (petrogenic sources). IP is a marker of diesel combustion and could tell the type of vehicle fuel. The IP/(IP + BghiP) ratio ranged between 0.37 to 0.50, respectively. These results suggest that PAHs are derived from mixed sources of vehicular exhaust and biomass combustion. Similarly the value of BaA/(BaA + Chr) ratio has been reported to vary between 0.39 and 0.64 for diesel emissions and between 0.22 and 0.5 for gasoline emissions [35]. Though the emissions from coal burning this ratio has been observed to be 0.50 [36]. In the present study, this ratio is 0.39 which can be attributed to vehicular emissions. The vehicular influence can further be assessed from Phen/(Phen + Anth) ratio whose value of 0.79 is comparable to values reported for diesel, coal and crude oil burning and gasoline emissions [37]. The Ant/(Ant + Phen) ratio < 0.1 petroleum sources and a ratio > 0.1 indicated that combustion sources dominated (in this study the ranges between 0.17 to 0.28). The ratio of BaP/(BaP + Chr) with its value 0.61 again indicates towards contributions from diesel emissions. The BaP/(BaP + BeP) ratio is approximately 0.50 for fresh particulate emissions [38]. The mean ratios of BaP/(BaP + BeP) among the four seasons in our study ranged from 0.26 to 0.67 (Table-3) indicating that the sample was from fresh particulate emissions. The mean ratios of BghiP/BeP for winter, summer, southwest monsoon and northeast monsoon in our study were 1.38, 2.54, 1.10 and 1.43, respectively (Table-3).

Principal component analysis (PCA): PCA was conducted in addition to diagnostic ratios on each set of data. The inference of PCA is as follows: The main PAHs contributor was vehicular emission related to both heavy and light traffic alone with incomplete combustion of various fuels. PCA was applied to all four seasons. The principal components (PCs) with eigen values greater than 0.8 were retained as they provided a reasonable physical interpretation of sources. The principal components were interpreted on the basis of their loadings.

TABLE-3
DIAGNOSTIC RATIOS

Diagnostic ratios	Winter	Summer	Southwest monsoon	Northeast monsoon	Seasonal average
Flt/ (Flt + Pyr)	0.35	0.21	0.32	0.35	0.31
Phen/(Phen + Anth)	0.76	0.72	0.84	0.80	0.78
IP/(IP + BghiP)	0.50	0.46	0.37	0.47	0.45
BaP/(BaP + Chy)	0.60	0.65	0.44	0.62	0.58
BaA/(BaA + Chy)	0.43	0.44	0.24	0.40	0.38
Ant/(Ant+Phe)	0.24	0.28	0.16	0.20	0.22
BaA/(BaA + Bep)	0.61	0.40	0.38	0.55	0.48
BghiP/BeP	1.38	2.54	1.10	1.43	1.61

Factor loadings greater than 0.5 were considered statistically significant. The factor profiles were constructed on the basis

of factor loadings (Table-4). In summer (Fig. 4b), the total variability was explained by two factors accounting for 89.27 %.

TABLE-4
FACTOR PATTERNS OF PRINCIPAL COMPONENTS (PC) 1 AND 2, FOR INDIVIDUAL PAHs FROM TIRUCHIRAPPALLI, INDIA

PAHs	Southwest monsoon		Northeast monsoon		Winter		Summer	
	PC 1	PC 2	PC 1	PC 2	PC 1	PC 2	PC 1	PC 2
Nap	0.70	-0.54	-2.03	-0.14	-2.21	-0.15	-0.90	-0.54
Acpy	-1.83	-0.33	-2.37	-0.12	-2.53	0.00	-1.70	-0.60
Acp	-2.64	-0.20	-2.47	-0.18	-2.50	-0.06	-1.63	-0.70
Flu	-2.26	-0.21	-2.40	-0.16	-2.53	0.01	-1.69	-0.61
Phe	0.83	-0.19	-1.43	-0.04	-1.40	0.08	0.13	-0.56
Ant	-2.28	-0.11	-2.29	-0.16	-2.37	0.02	-1.37	-0.62
Flua	-0.13	-0.11	-0.66	0.21	-0.14	0.46	0.16	-0.61
Pyr	2.27	2.20	0.97	0.56	2.42	1.40	6.30	-1.14
BaA	-1.32	-0.33	-0.35	0.53	-0.20	-0.08	-0.56	-0.32
Chr	2.60	-1.83	0.65	0.64	0.83	-0.21	-0.17	-0.20
BbikF	1.48	-1.20	1.40	0.11	1.43	-0.38	-0.33	0.14
BeP	1.64	-0.98	1.66	-0.05	0.97	-1.45	-0.27	0.25
BaP	0.97	0.40	3.31	0.81	3.11	-0.19	0.86	0.43
IP	-0.13	1.46	3.27	-0.98	2.76	0.12	0.54	1.54
BghiP	2.05	1.27	3.60	-0.64	2.98	-0.27	1.15	1.99
DBA	-1.95	0.71	-0.86	-0.40	-0.62	0.71	-0.51	1.54
Eigen value	3.29	1.04	4.72	0.23	4.51	0.34	3.60	0.86
Variance (%)	65.76	20.84	94.42	4.53	90.17	6.83	71.98	17.29
Cumulative (%)	65.76	86.61	94.42	98.94	90.17	97.00	71.98	89.27

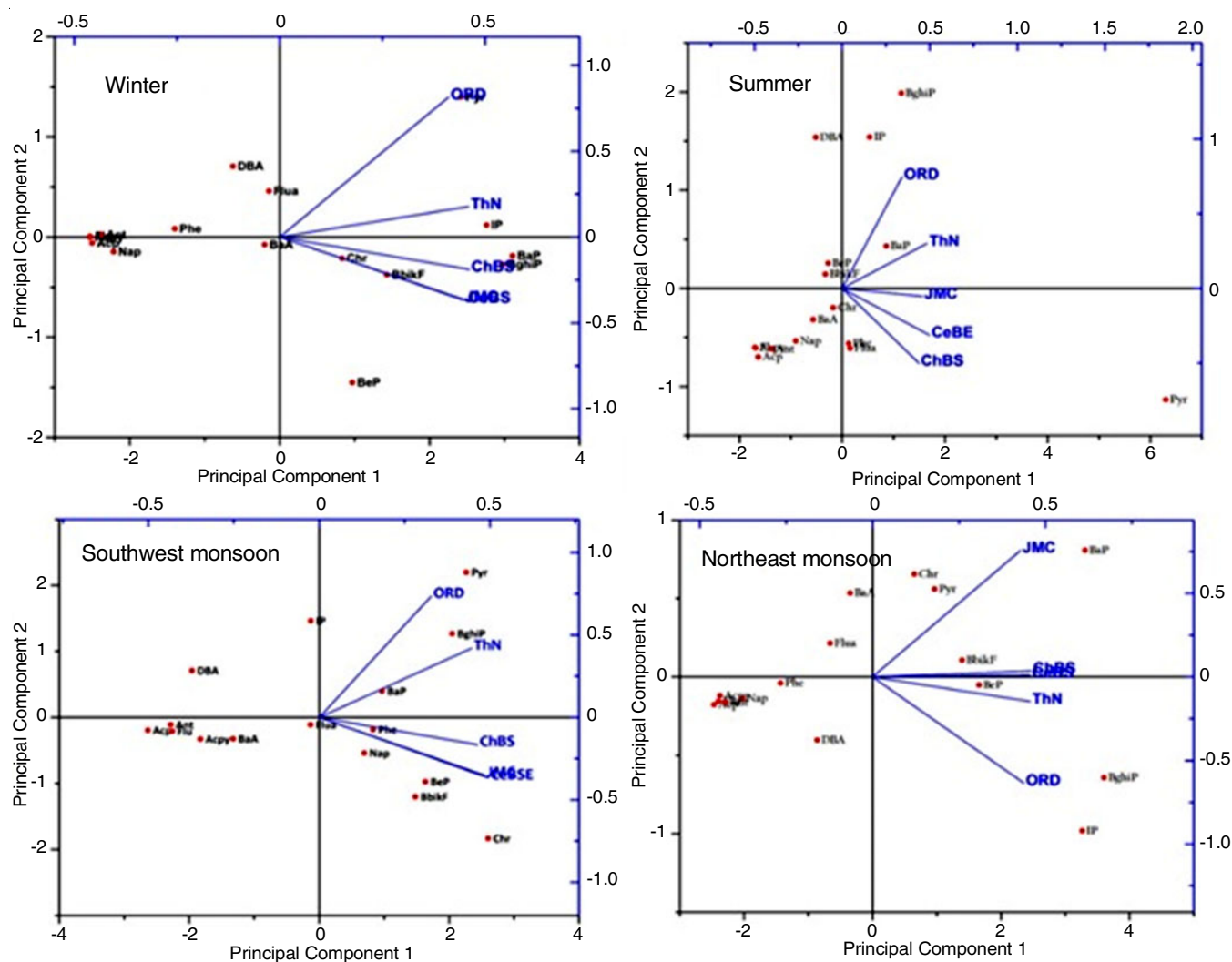


Fig. 4. Principal component analysis (a) winter, (b) summer, (c) southwest monsoon and (d) northeast monsoon

Factor 1, accounted for total variance of 71.98 %, was loaded with Pyr and Bap. This combination suggested vehicular emissions inclusive of petrol- and diesel-driven engines as the major sources [22,27]. Factor 2 accounted for 17.29 % of the total variance with IP, DBA and BghiP, which could be contributed from wood and rubbish combustion. During summer, the higher loadings of Pyr are obtained in Factor 1, indicating a potential pollution of wood and rubbish combustion. For winter season (Fig. 4a), PCA identified two factors accounting for 97.10 % of total variance. Factor 1 loaded with Pyr, Chr, BbjkF, Bep, BaA, BghiP and IP accounted for 90.17 % of variance. Emissions from diesel- and gasoline-powered vehicles were identified as probable sources of these PAHs [39]. Factor 2 consisted of DBA with representation of 6.83 % of total variance. In north-east monsoon (Fig. 4d), the total variance of 98.94 % was explained only one factor which was highly loaded with Pyr, Chr, BbjkF, Bep, BaA, BghiP, and IP accounting for 94.42 % total variability primarily associated with gasoline and diesel vehicles. In southwest monsoon, among the total variance of 86.61 %, factor 1 accounted for 65.76 %, total variability with 65.76 %, (Fig. 4c). This factor could be attributed to the gasoline and diesel vehicle emissions with high molecular weight PAHs. The second factor with 20.84 % total variance grouped as IP and DBA which could be contributed from wood and rubbish combustion. The principle component analysis and diagnostic ratio showed that the major sources for polycyclic aromatic hydrocarbons in the prescribed sites are vehicular emissions followed by off-road combustion sources such as wood and solid waste sources for airborne PAHs.

Conclusion

Sixteen priority polycyclic aromatic hydrocarbons listed by USEPA associated with PM_{2.5} were identified and quantified at five sites namely Central bus stand, Chathiram bus stand, Jamal Mohamed College, Orchard School and Thillai Nagar located in Tiruchirappalli city, India. The most abundant PAHs were the ones with higher molecular weight emitted significantly by incomplete combustion in the mentioned areas. Seasonal variation was observed in the total PAHs and BaP_{eq} as well as the individual compounds were lower in warm months than in cold months. Annual average level of BaP in five sampling site figured between 1.43 and 4.22 ng/m³, exceeding the NAAQS (2009) annual average of 1 ng/m³. Overall assessment reveals that the total particulate PAH concentrations are present at alarming level in Tiruchirappalli city, India. The principle component analysis and diagnostic ratio shows that the major sources for polycyclic aromatic hydrocarbons in the prescribed sites are vehicular emissions followed by off-road combustion sources such as wood and solid waste, sources for airborne PAHs. The results obtained reflect the deterioration in air quality in the urban area of Tiruchirappalli as a result of high population and vehicle fleet growth. This suggests that establishing strategies oriented to the reduction of atmospheric emissions is required, including the modernization of road transport and planning infrastructure, fuel quality, road network, among other strategies. These observed results provide a platform to implement measures to control the emission of particulate matters and thus prevent local and national wide air pollution confirming to regulations to improve environmental health.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- S. Gulia, S.M. Shiva Nagendra, M. Khare and I. Khanna, *Atmos. Pollut. Res.*, **6**, 286 (2015); <https://doi.org/10.5094/APR.2015.033>.
- J. Liu, R. Man, S. Ma, J. Li, Q. Wu and J. Peng, *Mar. Pollut. Bull.*, **100**, 134 (2015); <https://doi.org/10.1016/j.marpolbul.2015.09.014>.
- J.J. Swanson, W.F. Watts, R.A. Newman, R.R. Ziebarth and D.B. Kittelson, *Environ. Sci. Technol.*, **47**, 4521 (2013); <https://doi.org/10.1021/es304971h>.
- A. Valavanidis, K. Fiotakis and T. Vlachogianni, *J. Environ. Sci. Health Part C*, **26**, 339 (2008); <https://doi.org/10.1080/10590500802494538>.
- P. Perez, E. Fernandez and R. Beiras, *Water Air Soil Pollut.*, **209**, 345 (2010); <https://doi.org/10.1007/s11270-009-0203-9>.
- V. Singla, T. Pachauri, A. Satsangi, K.M. Kumari and A. Lakhani, *Polycycl. Aromat. Compd.*, **32**, 199 (2012); <https://doi.org/10.1080/10406638.2012.657740>.
- J. Niu, Dai H., J. Xu and Z. Shen, *J. Hazard. Mater.*, **248–249**, 254 (2013).
- X.T. Wang, Y. Miao, Y. Zhang, Y.-C. Li, M.-H. Wu and G. Yu, *Sci. Total Environ.*, **447**, 80 (2013); <https://doi.org/10.1016/j.scitotenv.2012.12.086>.
- S.M. Horaginamani and M. Ravichandran, *Indian J. Environ. Ecolplan*, **16**, 189 (2009).
- L. Xu, X. Chen, J. Chen, F. Zhang, C. He, J. Zhao and L. Yin, *Atmos. Res.*, **104–105**, 264 (2012); <https://doi.org/10.1016/j.atmosres.2011.10.017>.
- M.S. Alam, J.M. Delgado-Saborit, C. Stark and R.M. Harrison, *Atmos. Environ.*, **77**, 24 (2013); <https://doi.org/10.1016/j.atmosenv.2013.04.068>.
- B. Zielinska, J. Sagebiel, W.P. Arnott, C.F. Rogers, K.E. Kelly, D.A. Wagner, J.S. Lighty, A.F. Sarofim and G. Palmer, *Environ. Sci. Technol.*, **38**, 2557 (2004); <https://doi.org/10.1021/es030518d>.
- G.C. Fang, Y.S. Wu, J.C. Chen, P.P.C. Fu, C.N. Chang, T.T. Ho and M.H. Chen, *Chemosphere*, **60**, 427 (2005); <https://doi.org/10.1016/j.chemosphere.2004.12.034>.
- Y. Liu, S. Tao, Y. Yang, H. Dou, Y. Yang and R.M. Coveney, *Sci. Total Environ.*, **383**, 98 (2007); <https://doi.org/10.1016/j.scitotenv.2007.05.008>.
- G. Wang, L. Huang, Xin Zhao, H. Niu and Z. Dai, *Atmos. Res.*, **81**, 54 (2006); <https://doi.org/10.1016/j.atmosres.2005.11.004>.
- F. Halek, M. Kianpour-rad and A. Kavousi, *Environ. Chem. Lett.*, **8**, 39 (2010); <https://doi.org/10.1007/s10311-008-0188-4>.
- A. Masih, R. Saini, R. Singhvi and A. Taneja, *Environ. Monit. Assess.*, **163**, 421 (2010); <https://doi.org/10.1007/s10661-009-0846-4>.
- S.S. Park, Y.J. Kim and C.H. Kang, *Atmos. Environ.*, **36**, 2917 (2002); [https://doi.org/10.1016/S1352-2310\(02\)00206-6](https://doi.org/10.1016/S1352-2310(02)00206-6).
- R. Mohanraj and P.A. Azeez, *Resonance J. Sci. Educ.*, **8**, 20 (2003).
- R. Mohanraj, S. Dhanakumar and G. Solaraj, *The Scientific World J.*, **2012**, Article ID 980843 (2012); <https://doi.org/10.1100/2012/980843>.
- T. Ohura, T. Amagai, M. Fusaya and H. Matsushita, *Environ. Sci. Technol.*, **38**, 77 (2004); <https://doi.org/10.1021/es030512o>.
- A.M. Caricchia, S. Chiavarini and M. Pezza, *Atmos. Environ.*, **33**, 3731 (1999); [https://doi.org/10.1016/S1352-2310\(99\)00199-5](https://doi.org/10.1016/S1352-2310(99)00199-5).
- E. Sanderson, *Atmos. Environ.*, **38**, 3417 (2004); <https://doi.org/10.1016/j.atmosenv.2004.03.026>.

24. A. Eiguren-Fernandez, A.H. Miguel, J. Froines, R.S. Thurairatnam and E.L. Avol, *Aerosol Sci. Technol.*, **38**, 447 (2004); <https://doi.org/10.1080/02786820490449511>.
25. J. Li, G. Zhang, X.D. Li, S.H. Qi, G.Q. Liu and X.Z. Peng, *Sci. Total Environ.*, **355**, 145 (2006); <https://doi.org/10.1016/j.scitotenv.2005.02.042>.
26. J.H. Tan, X.H. Bi, J.C. Duan, K.A. Rahn, G.Y. Sheng and J.M. Fu, *Atmos. Res.*, **80**, 250 (2006); <https://doi.org/10.1016/j.atmosres.2005.09.004>.
27. H.S. Hong, H.L.G. Yin, X.H. Wang and C.X. Ye, *Atmos. Res.*, **85**, 429 (2007); <https://doi.org/10.1016/j.atmosres.2007.03.004>.
28. K. Karar and A.K. Gupta, *Atmos. Res.*, **81**, 36 (2006); <https://doi.org/10.1016/j.atmosres.2005.11.003>.
29. K. Ravindra, R. Sokhi and R. Vangrieken, *Atmos. Environ.*, **42**, 2895 (2008); <https://doi.org/10.1016/j.atmosenv.2007.12.010>.
30. J.F. Müller, D.W. Hawker and D.W. Connell, *Chemosphere*, **37**, 1369 (1998); [https://doi.org/10.1016/S0045-6535\(98\)00119-2](https://doi.org/10.1016/S0045-6535(98)00119-2).
31. K.H. Kim, S.A. Jahan, E. Kabir and R.J. Brown, *Environ. Int.*, **60**, 71 (2013); <https://doi.org/10.1016/j.envint.2013.07.019>.
32. C. Nisbet and P. LaGoy, *Regul. Toxicol. Pharmacol.*, **16**, 290 (1992); [https://doi.org/10.1016/0273-2300\(92\)90009-X](https://doi.org/10.1016/0273-2300(92)90009-X).
33. A. Katsoyiannis, A.J. Sweetman and K.C. Jones, *Environ. Sci. Technol.*, **45**, 8897 (2011); <https://doi.org/10.1021/es202277u>.
34. R.J. De La Torre-Roche, W.-Y. Lee and S.I. Campos-Díaz, *J. Hazard. Mater.*, **163**, 946 (2009); <https://doi.org/10.1016/j.jhazmat.2008.07.089>.
35. M.A. Sicre, J.C. Marty, A. Saliot, X. Aparicio, J. Grimalt and J. Albaiges, *Atmos. Environ.*, **21**, 2247 (1987); [https://doi.org/10.1016/0004-6981\(87\)90356-8](https://doi.org/10.1016/0004-6981(87)90356-8).
36. M.B. Yunker, R.W. Macdonald, R. Vingarzan, R.H. Mitchell, D. Goyette and S. Sylvestre, *Org. Geochem.*, **33**, 489 (2002); [https://doi.org/10.1016/S0146-6380\(02\)00002-5](https://doi.org/10.1016/S0146-6380(02)00002-5).
37. C. Alves, C. Pio and A. Duarte, *Atmos. Environ.*, **35**, 5485 (2001); [https://doi.org/10.1016/S1352-2310\(01\)00243-6](https://doi.org/10.1016/S1352-2310(01)00243-6).
38. C. Oliveira, N. Martins, J. Tavares, C. Pio, M. Cerqueira, M. Matos, H. Silva, C. Oliveira and F. Camões, *Chemosphere*, **83**, 1588 (2011); <https://doi.org/10.1016/j.chemosphere.2011.01.011>.
39. R.K. Larsen and J.E. Baker, *Environ. Sci. Technol.*, **37**, 1873 (2003); <https://doi.org/10.1021/es0206184>.