Bull Environ Contam Toxicol (2011) 87:330–335
DOI 10.1007/s00128-011-0349-1

PM 2.5 and PAH Concentrations in Urban Atmosphere of Tiruchirappalli, India

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Received: 1 February 2011 / Accepted: 20 June 2011 / Published online: 29 June 2011

Abstract Airborne PM 2.5 and polycyclic aromatic hydrocarbons (PAHs) bound to it were determined from March 2009 to February 2010 at different locations in Tiruchirappalli City, Southern India using fine particulate sampler and high performance liquid chromatography. Average $\sum$9 PAHs concentrations at four sampling stations were 333.7, 202.6, 265.9, and 232.7 ng/m^3, respectively. Highest concentration of PAHs was observed during northeast monsoon season (301.5 ng/m^3) and lowest in southwest monsoon (216 ng/m^3). Low and medium molecular weight PAHs such as phenanthrene, anthracene, benzo(a)anthracene and chrysene were observed in all seasons. Principal compound analysis revealed gasoline and diesel vehicular emissions as major sources for PAHs compounds.

Keywords Urban air pollution · Fine particulates · Polycyclic aromatic hydrocarbons · Source apportionment

As the major mega-cities and metropolis in India reaches saturation point due to economic boom, the spill out effect fosters a rapid growth of tier II cities (cities with population less than 1 million). As a consequence these cities are noticed with significant rise in urbanization, industrialization and on-road/off-road emission sources resulting in air quality deterioration. Poor infrastructure and fuel quality further aggravates air pollution. Among air pollutants, fine particles and PAHs associated with this fraction are well known for its toxic properties. A number of them are either known or suspected carcinogens. In addition, PAHs have also been reported to have reproductive, developmental, hemato-, cardio-, neuro-, and immuno-toxicities in humans and laboratory animals (ATSDR 1995; IARC 1983).

PAHs are released into the atmosphere as a complex mixture of compounds during incomplete combustion of organic matter. Higher concentrations PAH in air are reported in urban environment due to vehicular traffic and the scarce dispersion of the atmospheric pollutants (Callen et al. 2011; Liu et al. 2007). As the density of population in the cities remains high, more number of people have the risk of exposure to PAHs through inhalation and ingestion (Bostrom et al. 2002; Ramesh et al. 2004).

High levels of ambient atmospheric PAHs were observed in developing countries particularly in India. During 2009, in Agra city, India, total suspended particles and $\sum$14 PAHs recorded up to 269 ng/m^3 and 400 μg/m^3 (Rajput and Lakhani 2009). In Lucknow city, Particulate bound PAHs were observed in the range of 0.42–204.17 ng/m^3 (Singh et al. 2008). In Delhi, Sharma et al. (2007) observed mean concentrations of 668 and 672 ng/m^3 total PAHs in the years 2002 and 2003, respectively. It is also alarming to note that annual PAH emissions from Asian countries were 290 Gg year^{-1}, with China and India contributing 114 and 90 Gg year^{-1} respectively. The proportion of high molecular weight PAH emission from India (3.60%) was significantly higher than the global average. Although experimental data on PAHs in the coarse particulate matter is scarcely available for few cities in India (Raiyani et al. 1993; Chattopadhyay et al. 1998; Kulkarni and Venkataraman 2000), trends of fine particulate bound PAHs are extremely limited.

To address this knowledge gap an attempt is made in Tiruchirappalli city lying between North Latitude 10 to 11–30', East Longitude 77–45' to 78–50', which is an

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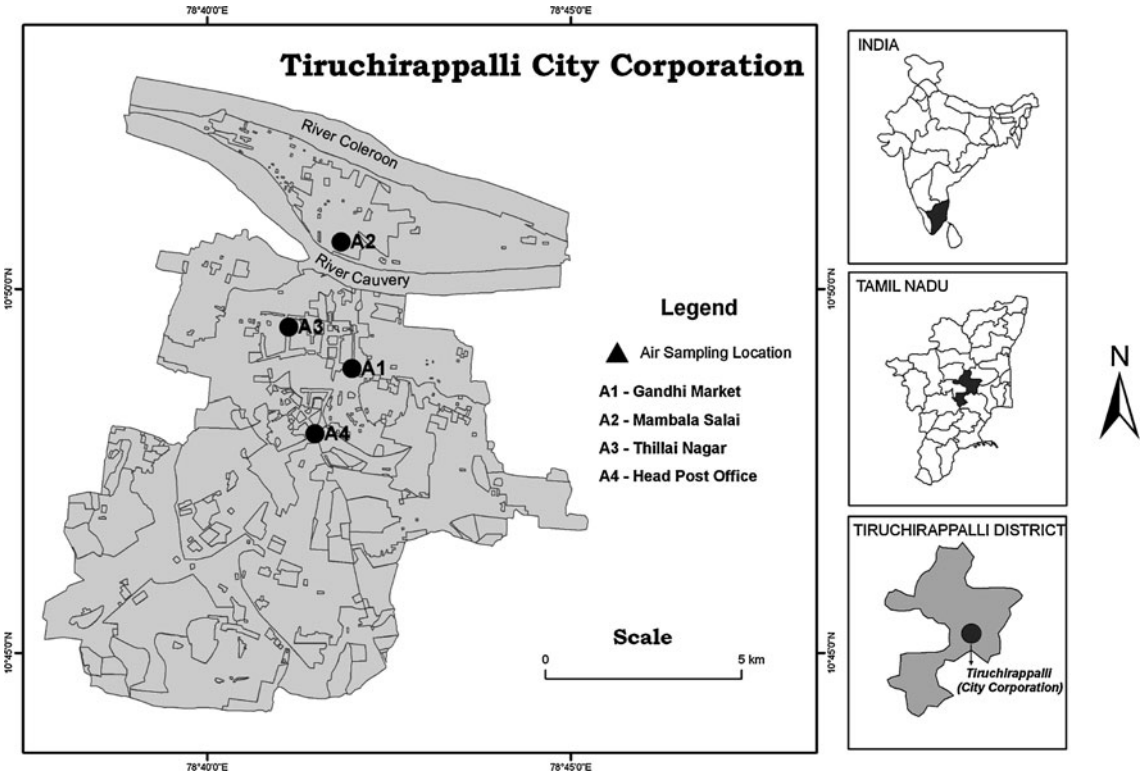

Fig. 1 The locations of sampling sites on the map of Tiruchirappalli city

ancient historical city. BHEL (Bharat Heavy Electricals Limited), the public sector giant, accounts for nearly three-fourth of the turnover of engineering industry in Tiruchirappalli. There are more than 300-odd metal fabricating industries, where about 1.5 lakhs tones of steel are being processed annually. Tiruchirappalli City had a population of 7,46,062 in the 2001 census within its municipal corporation. Total number of vehicles registered with the 'Regional Transport Authority' was 3,38,153 in 2006–2007. An unprecedented increase in urbanization, industrialization and automobiles are noticed in last 5 years. The purpose of this study was to assess airborne PM 2.5 fraction and PAHs in PM 2.5 in Tiruchirappalli city with emphasis on seasonal variation and principal component analysis.

Materials and Methods

Four air sampling sites were selected based on background activities (urban commercial, sub-urban residential and mixed commercial and residential) in Tiruchirappalli, India (Fig. 1). The protocol for installation of air samplers regarding height and distance from the source was followed as per USEPA guidelines. The meteorological parameters for the study period are given in Table 1. Fine particulate matter (PM 2.5) was collected using a Fine Particulate Sampler (Model: APM 550, Make: Envirotech, New Delhi, India) from March 2009 to February 2010 at monthly intervals. The sampling rate of the system was held constant at 1 m^3/h for 24 h. PM 2.5-laden PTFE membrane filters obtained after 24-h air sampling were subjected to PAH analysis. Several analytical techniques that have been used earlier were carefully considered for extraction efficiency, accuracy, detection limits, and cost, and finally, an appropriate method was evaluated. In the present investigation, PAH extraction and analysis were carried out as per modified Colombini et al. (1998) method. PTFE membrane filter carrying PM 2.5 was ultrasonically extracted by dichloromethane: methanol (60:40) mixture in a dark bottle for 2–3 times. The extracted solution was filtered through 0.2-μm PTFE filter and then redissolved in acetonitrile for high-performance liquid chromatography (HPLC) analysis. PAH standards obtained from SUPELCO were used to generate standard chromatogram for 11 PAH compounds. After required dilution, a standard was injected in HPLC (Make: Waters, USA) with PAH C18 column (5 μm 4.6 × 250 mm), and the compounds are determined in fluorescence detector (model: 2475). After standardization, the samples were injected for PAH analysis. Chromatographic peaks were identified by comparing retention times of samples with those of reference PAH compounds. List of PAHs analyzed is as follows: phenanthrene (phenan), anthracene (anth), benzo(a)anthracene

Table 1 Meteorological condition in Tiruchirappalli during the study period (March 2009–February 2010)

Month	Temperature (°C)	Humidity (%)	Wind speed (km/h)	Rain fall (cm)
March	29.03	57.03	6.97	0.0
April	31.23	57.10	9.23	0.0
May	32.48	54.87	15.35	0.0
June	32.03	54.60	19.53	0.0
July	31.61	56.48	28.97	0.0
August	30.81	51.45	17.90	0.8
September	30.67	56.87	15.97	0.0
October	29.61	57.16	8.29	0.0
November	26.50	81.40	8.90	2.3
December	25.19	78.94	12.61	0.9
January	25.39	70.03	10.16	0.0
February	26.79	62.14	7.57	0.0

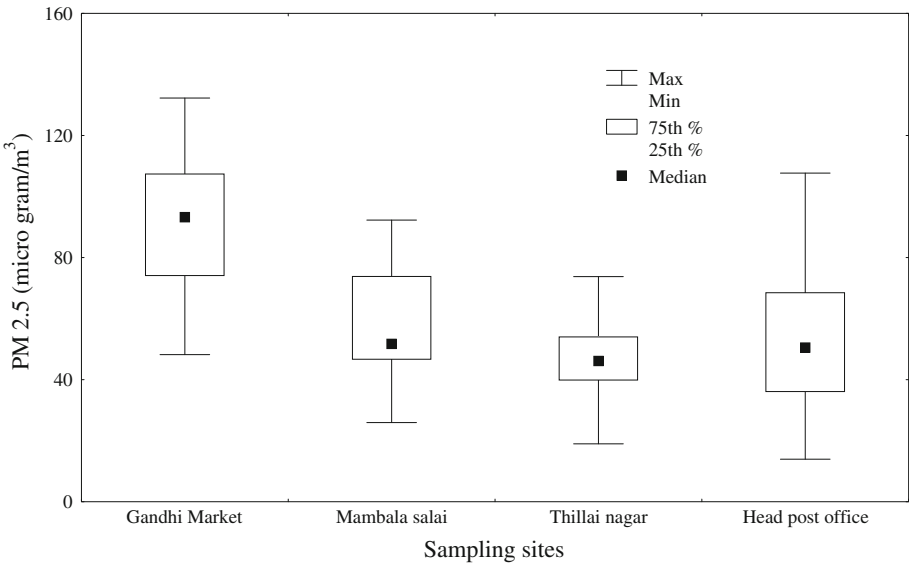

Fig. 2 Fine particulate matter concentration in select location in Tiruchirappalli, India

(baa), chrysene (chry), benzo(b)fluoranthene (Bbf), benzo(k)fluoranthene (bkf), benzo(a)pyrene (bap), indeno 1, 2, 3-cd pyrene (Icdp), and benzo(ghi)perylene (bghip; Supelco, USA). Results of PM 2.5 and particulate-bound PAH concentrations were subjected to statistical analysis including analysis of variance (ANOVA) and principal component analysis (PCA) using SPSS 11.0.

Results and Discussion

In Tiruchirappalli, PM 2.5 values varied between 13.9 and 132.3 μg/m^3 with an annual average of 63.4 μg/m^3 (Fig. 2). Although Tiruchirappalli is rated only as fourth largest city in Tamilnadu state, India, PM 2.5 values at Tiruchirappalli exceeded the National Ambient Air quality Standard Quality Standards (NAAQS) of 40 μg/m^3 and USEPA standard of 15 μg/m^3 on annual basis. Among the four sampling sites, urban hub station A1 (Gandhi Market) recorded comparatively higher the concentration of PM 2.5 level with an annual average of 93.2 μg/m^3. Gandhi Market is an important commercial zone often observed with high truck traffic. Sub-urban residential site A2 (Mambalasalai) showed the levels of fine particulate matter in the range between 25.9 and 92.3 μg/m^3. Analysis of variance (ANOVA) yielded statistically significant difference between sampling sites and seasons for fine particulate matter concentrations.

Annual average of the sum of 9 PAH concentrations observed in four sampling stations, i.e., Gandhi market, Mambala salai, head post office and Thillainagar, were 333.7, 202.6, 265.9, and 232.7 ng/m^3, respectively (Table 2). Maximum annual average of 333.7 ng/m^3 was recorded at Gandhi Market (urban commercial area) followed by another commercial area head post office (265.9 ng/m^3). In addition to vehicular traffic, regular

Table 2 Seasonal variation of PAH concentrations in Tiruchirappalli City, India (n = 48)

Sampling sites	Mean PAH concentrations (ng/m^3)									TPAHs
	PHENAN	ANTH	BaA	CHRY	BbF	BkF	BaP	BghiP	IcdP	
Winter season (December to February)										
Gandhi market	92.3	BDL	BDL	114.7	35.3	10.9	18.9	56.7	12.2	341
Mambalasalai	49.8	32.1	23.8	30.1	21.1	16.3	8.7	19.3	17.7	219
Thillainagar	BDL	112.6	BDL	10.5	12.9	BDL	BDL	BDL	BDL	136
Head post office	76.2	27.9	50.7	84.2	20.2	9.3	24.1	69.7	9.3	371.5
Summer season (March to May)										
Gandhi market	42.6	50.8	29.3	51.4	16.5	3.5	14.4	21.8	10.9	241.3
Mambalasalai	21.8	34.9	40	25.6	13.5	4	5.6	18.7	7.2	171.3
Thillai nagar	42.1	84.1	34.7	30.3	16.5	5	7.6	40.4	18.8	279.5
Head post office	35	100.1	58.7	37.7	18.7	5.6	5.6	54	5.5	320.8
Southwest monsoon (June to August)										
Gandhi market	70.9	BDL	BDL	43.4	38.1	17.9	21.1	59.9	16	267.4
Mambalasalai	40	30.9	21.8	24.4	12.4	6.8	12	22.3	31.2	201.7
Thillainagar	60.4	BDL	4.3	48.6	19.8	7	6.7	34.3	14.8	195.8
Head post office	28	92.8	7.2	21.1	5	3	9.4	20.3	12.2	198.9
Northeast monsoon (September to November)										
Gandhi market	91.8	49.2	51.9	101	40.7	16.9	44.6	68	23.4	487.5
Mambalasalai	51.9	23.5	9.4	23.9	30.8	18.6	17.2	17.4	31.1	223.8
Thillainagar	62.2	62	28.9	47.1	13.1	9.6	16.8	24.1	23.5	287.3
Head post office	52.6	67.4	6	29.7	9.3	2.8	20.2	14	5.4	207.4
Limit of detection of PAHs (μg/ml)										
LOD	0.0042	0.0014	0.006	0.0068	0.0056	0.0072	0.0095	0.0088	0.0065	–

BDL below the detectable limit, *LOD* limit of detection, *PHENAN* phenanthrene, *ANTH* anthracene, *BaA* benzo(a)anthracene, *CHRY* chrysene, *BbF* benzo(b)fluoranthene, *BkF* benzo(k)fluoranthene, *BaP* benzo(a)pyrene, *IcdP* indeno 1, 2, 3-cd pyrene, *BghiP* benzo(ghi)perylene, *TPAHs* total PAHs

practice of burning solid wastes also might have contributed to ambient PAH in Gandhi market. In general, three or more aromatic ring PAHs are mostly associated with particulate matter (Caricchia et al. 1999). In present study, predominant PAHs in all sampling stations were PHENAN, ANTH, CHRY and BghiP with an annual average of 50.8, 48.5, 43.9 and 33.6 ng/m^3, respectively. Higher level of PHENAN and ANTH in the particulate phase suggested significant contribution from gasoline emissions. Annual average level of BaP in four sampling sites figured between

Table 3 Site specific and seasonal wise mean molecular ratios of PAHs and their probable sources

Sampling stations	BaP/ (BaP + CHRY)	BaP/ BghiP	IcdP/ (IcdP + BghiP)	BaA/ (CHRY + BaA)	BghiP/ BaP	ANTH/ (PHENAN + ANTH)	PHENAN/ ANTH
Gandhi market	0.27	0.63	0.28	0.28	2.21	0.12	0.09
Mambala salai	0.30	0.41	0.40	0.34	1.94	0.43	0.19
Thillai nagar	0.21	0.30	0.27	0.24	3.21	0.41	0.06
Head post office	0.27	0.26	0.21	0.28	4.07	0.44	0.20
Summer	0.20	0.45	0.30	0.52	4.62	0.49	0.26
Southwest monsoon	0.29	0.30	0.40	0.13	3.40	0.21	0.1
Northeast monsoon	0.39	0.57	0.29	0.22	1.43	0.31	0.04
Winter	0.14	0.22	0.15	0.19	1.77	0.42	0.19

BaP benzo(a)pyrene, *CHRY* chrysene, *BghiP* benzo(ghi)perylene, *IcdP* indeno 1, 2, 3-cd pyrene, *BaA* benzo (a)anthracene, *PHENAN* phenanthrene, *ANTH* anthracene

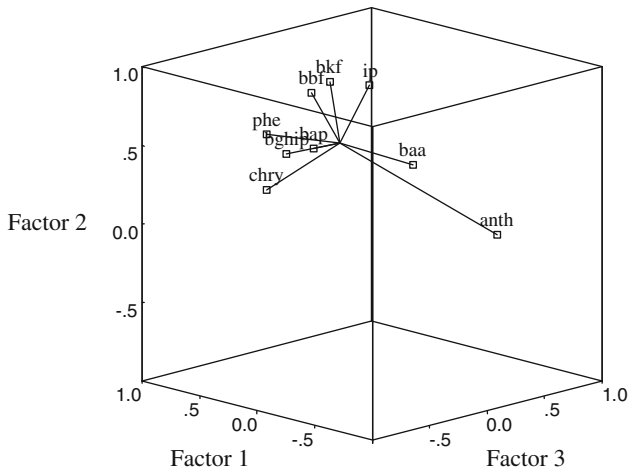

Fig. 3 Factor loadings of principal component analysis

8.5 and 25.3 ng/m^3, exceeding the NAAQS (2009) annual average of 1 ng/m^3.

PAH diagnostic ratio computation is one among the tool used to categorize emission sources based on the concentrations of specific PAH compounds or groups of PAHs. In the present study, site specific and seasonal wise PAH ratios was attempted (Table 3). Mean ratio of BaA/(CHRY + BaA) ranging between 0.24 and 0.34 in all sampling stations indicated catalyst cars as an important source (Scherer et al. 2000). Higher ratio (4.07) of BghiP/BaP in Head post office (urban site) hinted diesel powered vehicles emissions as a prime source of PAHs in this location. Ratio of BghiP/BaP observed in all four sampling sites in the city also indicated contribution by re-suspension of road dust (Rogge et al. 1993). The overall information and the above analysis of PAH diagnostic ratios point out that the emissions from diesel powered vehicles, road dust and catalyst equipped cars attributed to substantial contribution of PAHs in Tiruchirappalli City.

Principal component analysis (PCA) was also applied to identify emission sources of particulate bound PAHs. Figure 3 shows the loading of each variable on each factor and the communality of each variable accounted for in the analysis. PCA extracted three factors with variability accounting for 74.41% of the total variance. Factor 1 accounted for 31.71% of representation with high loadings of PHENAN, CHRY, BaP and BghiP suggesting diesel engine emissions as prominent sources (Rajput and Lakhani 2009). This also supported a general perception of growing manufacturing sector and concurrent rise in diesel driven trucks carrying manufacturing goods in Tiruchirappalli. The second factor accounted for 28.2% of total variance, with loadings of BbF, BkF and IcdP. This factor suggests possible contribution from vehicle emission (Li and Kamens 1993). Factor 3 yielded 14.5% of the total variance with ANTH and BaA loadings. Gasoline and diesel emissions are likely sources of factor 3 (Daisey et al. 1979).

Acknowledgments We thank Defence Research and Developmental Organization (DRDO), Government of India, for financial support.

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