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ScientEvents

ProScience 3 (2016) 111-116

ProScience

Conference Proceedings

2nd International Conference on Atmospheric Dust - DUST2016

Source apportionment of polycyclic aromatic hydrocarbons in urban atmosphere of South Delhi, India

Saurabh Sonwani

School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India
**sonwani.s19@gmail.com*

Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous persistence organic pollutants (POPs). Several PAHs are known toxic, mutagenic and carcinogenic compounds. Understanding the contributions of the various emission sources is critical to appropriately managing PAH levels in the environment. In the present study, PM_{10} samples were collected at two sampling sites (UA and CR) in Delhi during the period of monsoon and winter season from July 2013 to January 2014. The concentrations of 10 selected PAHs in aerosols were quantified for source apportionment analysis. Their total amount at CR ranged from 18 to 161 ngm^{-3} whereas at UA it varies from 15 to 116 ngm^{-3}. The sources of PAHs in Delhi were determined by using source apportionment methods (molecular diagnostic ratios). At CR, vehicular emissions in the form of diesel and gasoline exhaust were major emission sources. On the contrary, mixed type of sources (coal combustion, wood combustion and gasoline and diesel engine emissions) were the contributor of particulate PAHs at UA in Delhi. The results clearly indicate that the major PAHs emission sources in the Delhi are traffic emission, coal combustion, and wood combustion related sources. These sources are responsible for high levels of PAHs which draws attention towards immediate measures for PAHs control in Delhi.

Keywords: PAHs; Source apportionment; Diagnostic ratio; Delhi

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are the widespread lipophylic environmental pollutants (Haritash & Kaushik, 2009). PAHs are toxic, mutagenic and carcinogenic compounds that can be present in the environmental matrices (soil, air and water) and may cause health problems via several routes such as inhalation, ingestion and dermal contact (e.g., Tsapakis & Stephanou, 2003; Rengarajan et al., 2015). PAHs originate from both natural and anthropogenic sources after incomplete combustion of organic materials. Anthropogenic sources include combustion of fossil fuels, tobacco, and meat while natural

ISSN: 2283-5954
Selection and peer-review under responsibility of DUST2016 Scientific Committee
DOI:10.14644/dust.2016.018

sources include biomass burning, volcanic eruptions and diagenesis (Ravindra et al., 2008; Rengarajan et al., 2015). PAHs are usually more concentrated near urban and industrial areas where most of the chemicals are originated from anthropogenic emissions such as combustion of coal, wood petrol, diesel and industrial practices (e.g., Hyötyläinen & Oikari 2004). In the present study, the total particulate PAHs level were recognized whereas, Molecular Diagnostic Ratios were used for source apportionment analysis of identified PAHs. The aim was to provide a better understanding about the PAHs pollution sources in order to contribute to air quality policies, which could further decrease damaging effects on human health.

2. Materials and methods

2.1 Sampling locations and campaign

Delhi is located in the northern part of India (28°24'17" and 28°53'00" N; 76°50'24" and 77°20'37" E), between the Thar Desert of Rajasthan to the west, the central hot plains to the south, the cooler hilly region to the north and east (Fig. 1a). The study was performed at two sites: University Campus Area (UA) and Cross Road site (CR). The first sampling site was away from the city and receives the city emission due to the prevailing wind direction in most part of the year, while second one was mostly influenced by vehicle traffic due to the closeness traffic intersection point (150 m) containing both heavy and light duty vehicles.

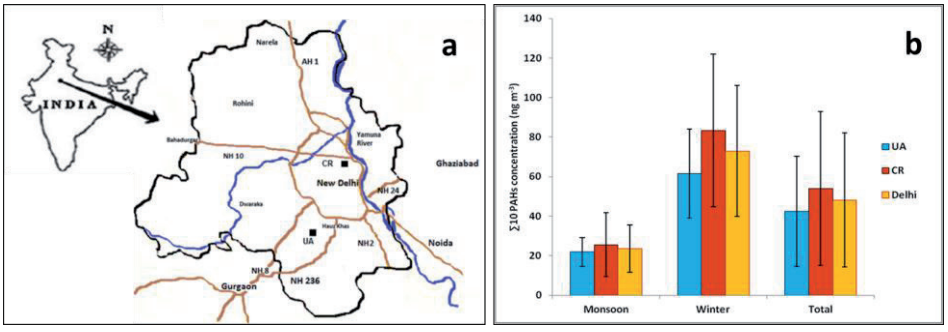

Fig. 1. (a) Map of the study area showing sampling sites; (b) Seasonal and spatial distribution of the $\sum_{10}$ PAHs (ng m^{-3}) for UA, CR, and Delhi

Respirable Dust Sampler (Model MLRDS-002, Mars Bio-analytical Pvt. Ltd; 1.1 m^3/min), provided with a PM_{10} cut off and located 15 m from the ground, was used to collect particulates over Whatman GF/A (8″×10″) glass fibre filters (GFFs) (precombusted at 450 °C for 12 h). Samples were collected on weekly basis and the time of sampling was 24 hrs. Total sampling period covered two seasons (monsoon and winter) in year of 2013-14; a total of 27 and 28 samples were collected at CR and UA sites, respectively. PM_{10} mass concentration was determined gravimetrically by weighting the filters, before and after sampling in a microbalance (accuracy 10 mg), once the filters were conditioned in desiccators.

2.2 PAH analysis

PAHs were extracted using ultrasonication (Sonicator 3000; Misonix Inc., USA) using toluene as solvent. Silica gel columns were used to remove impurities. HPLC system (Waters, USA; Model 510) equipped with a tunable absorbance UV detector (254 nm) was used for PAHs determination. The total targeted PAHs in the present study are the following: fluoranthene (Flan) and pyrene (Pyr), benz[a]anthracene (B[a]A) and chrysene (Chry), benz[b]fluoranthene (B[b]F), benz [k]fluoranthene (B[k]F), benz[a]pyrene (B[a]P), dibenz[a,h]anthracene (DB[ah]A), benz[ghi]perylene (B[ghi]P), and indeno[1,2,3-cd]pyrene (IP).

To avoid uncertainty in the measured concentration of particulate PAHs, the low molecular weight (two and three ring) PAHs were not considered for calculation of total PAHs and Diagnostic Ratio as they are very volatile in nature. In case of four-ring PAHs, they also partitioned to gas phase up to a significant fraction (Pitts and Pitts, 2000). In contrast to the low molecular weight PAHs, five- and six-ring PAHs are basically exist in the particulate phase due to their low volatile nature.

The aim of the present study is to report the particulate mass fraction of PAHs and related source apportionment to improve air quality policies, which could reduce harmful effects on human health.

3. Results and discussion

3.1 PM_{10} spatio-temporal variations

The mean PM_{10} variation at University Campus (UA) and Cross Road site (CR) was 225.95 ± 84.38 and 158.80 ± 83.33 μg m^{-3} respectively. The overall mean of PM_{10} at Delhi (mean of two sites) was193.12 ± 89.59 μg m^{-3}, which is more than 3 times the annual PM_{10} National Ambient Air Quality Standard (NAAQS; 60 μg m^{-3}) (NAAQS, 2009) and more than 9 times the annual PM_{10} standard (20 μg m^{-3}) set by the World Health Organization (WHO, 2006). The high concentration of PM_{10} at the UA as compared to the CR site can be explained by the nearness of the construction site to the university sampling area. In case of seasonal distribution author found the high concentration of PM_{10} in winter (288 ± 76.83 μg m^{-3} for UA and 220.39 ± 46.83 μg m^{-3} for CR) as compared to the monsoon season (208 ± 37.15 μg m^{-3} for UA and 84.89 ± 48.93 μg m^{-3} for CR) at both the sites, which could be attributed by lowering in mixing height and calm conditions leads to the lower dispersion of the particulate matter in winter season and precipitation scavenging during monsoon season (Seinfeld and Pandis, 2006) at both the sites.

3.2 Level, spatial and seasonal variation of atmospheric PAHs

PAHs concentration in Delhi and their seasonal and spatial variation are mentioned in the Fig. 1b. The overall mean $\sum_{10}$ PAHs concentration in Delhi was found high (48.17 ± 33.95 ng m^{-3}) and it was 48 times higher than NAAQS standard i.e. 1 ng m^{-3}. While the site specific mean PAHs level was 42 and 54 times higher than NAAQS standard at UA and CR site respectively. Present study found that the mean PAHs concentration of two different locations in Delhi was 48.17±33.95 ng m^{-3}. Fig. 1b reports the seasonal variation of PAHs at both the sites. As compared to the monsoon season, winter season had high PAHs concentration at both the sites; it was 61.56 ± 22.47 and 83.47 ± 38.66 ng m^{-3} for winter season at UA and CR sites, while 21.87 ± 7.24 and 25.52 ± 16.18 ng m^{-3} for monsoon

season at UA and CR sites, respectively. The high concentration of the PAHs at both the sites in Delhi can be due to lower mixing height, and calm atmospheric conditions leading to the lower dispersion of the pollutants. This is due to the cold start of vehicle (Ludykar et al. 1999) and local biomass burning for heating purpose during winter season. The low concentration of the PAHs during the monsoon season could be attributed by wet scavenging of the pollutants during rain events (Seinfeld and Pandis, 2006).

Several authors also reported that many organic pollutants at low temperature, low rate of photolysis, and low dispersion conditions are responsible for the higher level during winter season (e.g., Li et al., 2008; Caricchia et al., 1999). Traffic congestion due to poor visibility conditions from fog and haze is another factor responsible for PAHs increase during winter time (e.g., Rajput and Lakhani, 2010). These PAHs levels related to the cold and warm conditions were also reported by other authors (e.g., Holoubek et al., 2007; Chen et al., 2009) under the influence of meteorological conditions and high emission of PAHs during some anthropogenic activity like domestic heating during cold season.

3.3 Source apportionment of PAHs by Diagnostic ratios

PAHs diagnostic ratios have been used for the identification of several emission sources such as diesel and gasoline (Ravindra et al., 2008), burning of biomass, wood and oil processing products (Yunker et al., 2002). PAH isomer pair ratios also explain intra source unevenness but inter source evenness (Galarneau, 2008). The PAHs profile for a particular source depends on the process of their production (Manoli et al., 2004) such as low temperature procedures (e.g., Wood/biomass burning) responsible for the production of low molecular weight PAHs, while high temperature procedures (combustion of fuels in engines) are responsible for production of high molecular weight PAHs (Mostert et al., 2010). The PAHs ratios with their source signatures reported are reported in Table 1. Ratios of B[a]A/B[a]A + Chry indicated toward combustion sources of PAHs. Flan/Flan + Pyr ratio indicated coal or wood combustion. Ratios of IP/B[ghi]P and IP/IP + B[ghi]P indicated diesel emissions from vehicular sources and emission from coke/wood burning. B[b]F/B[k]F ratios pointed towards emissions related to the vehicles and smelters. B[a]P/B[ghi]P ratio related with coal combustion source of PAHs. BaP/(BaP+Chry) ratio indicated towards traffic and pyrogenic sources. Another B[b]F/B[k]F ratio pointing towards the smelters related emission sources.

Seasonal distribution of the PAHs sources, considering different PAHs isomer ratio such as BaP/(BaP+Chry) and Flan/(Flan+Pyr), indicate traffic, pyrogenic and fossil fuel emission source at CR site and it can be supported by the nearness of the industrial area and high speed winds in the monsoon seasons in Delhi. In case of the UA site, it had mixed pollution sources (combustion/ gasoline/coke) due to prevailing wind direction in Delhi (from the north and northwest except during the monsoon season that is characterized by easterly or south-easterly winds) as discussed in earlier study (Sarkar and Khillare, 2013).

In case of winter season, Flan/Flan + Pyr and B[a]P/B[ghi]P confirmed the coal/wood emission sources and can be explained on the basis of local residential heating activities. Traffic emission sources were confirmed by BaP/(BaP + Chry) and IP/(IP + B[ghi]P) ratios. In the case of UA site, the data (BaP/(BaP+Chry) pointing towards pyrogenic, fossil fuel and biomass burning sources which can be explained on the basis of local emission sources in campus area such as wood/coal burning used for local heating purpose. It can be also

supported by the fuel used in the canteen and mess present inside the university area. Flan/Flan+Pyr also pointing towards coal combustion related sources in UA site. Overall, PAH isomer diagnostic ratios at UA site pointing towards mixed pollution sources (vehicular, fossil fuel and coal combustion) in Delhi and could be attributed on the basis of prevailing winds directions. On the other hand, CR site is characterized by the presence of vehicle, coal combustion and smelter related emission sources due to the presence of gasoline and diesel powered motor vehicles and nearness of coal power plant and smelting industries.

4. Conclusion

The present study report evidences that the cross road site had higher atmospheric PAHs concentration as compared to the university area due to its nearness to the traffic point and industrial location. Winter season had high PAHs concentration at both the locations in Delhi. Source apportionment study found that Delhi was very much polluted at the time of sampling due to traffic emission and coal, wood burning and gasoline, and diesel engine emission sources. The high concentration of the PAHs and its emission sources pointing towards high health risk to the people living in the Delhi and it needs attention of policy makers to take immediate action to make the Delhi healthy and clean.

Table 1. Diagnostic PAHs ratios for ambient PM_{10} and particulate source emission

	CR		UA		
Molecular diagnostic ratios	**M**	**W**	**M**	**W**	**Ranges and possible sources**
B[a]A/B[a]A+Chry	0.71	0.35	0.72	0.62	Petroleum (<0.2), Petroleum/combustion (0.2–0.35), Combustion (>0.35). After Yunker et al. (2002)
Flan/Flan+Pyr	0.79	0.54	0.49	0.55	Petroleum (<0.4)*, Gasoline (0.4)** and Coal/wood (>0.5)*. After Yunker et al. (2002) (*) and Simcik et al. (1999) (**)
IP/IP+B[ghi]P	0.32	0.46	0.39	0.31	Gasoline (0.22), Diesel (0.5), Petroleum (1.3). After Yassaa et al. (2001)
B[a]A/Chry	9.37	0.61	2.65	2.27	Vehicles (0.53), Smelters (0.6), Wood (0.79), Coal/coke (1.11) After Dickhut et al. (2000)
IP/B[ghi]P	0.56	1.19	0.72	0.71	Wood (0.29)*, Gasoline (0.4)**, Diesel (1)**, coal/coke (1.09)*; After Dickhut et al. (2000) (*) and (**) Caricchia et al. (1999)
B[b]F/B[k]F	6.29	2.45	1.22	3.16	Wood (0.92), Vehicles (1.26) and Smelters (2.69) After Dickhut et al. (2000)
B[a]P/B[ghi]P	0.82	1.26	0.83	0.58	Vehicles (0.3–0.78) and Coal (0.9–6.6). After Simcik et al. (1999)
Pyr/B[a]P	1.84	2.40	1.38	0.86	Diesel engine (~10) and Gasoline engine (~1). After Ravindra et al. (2008)
BaP/BaP+ Chry	0.59	0.60	0.74	0.51	Traffic source (≥ 0.6)*, Pyrogenic source and Fossil fuel/biomass combustion (>0.35)**. After Tasapakis and Stephanou (2002) (*) and Kamal et al. (2016) (**)

5. Acknowledgement

The author acknowledges the award of fellowship from UGC during research period.

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