

Emission sources, Characteristics and risk assessment of particulate bound Polycyclic Aromatic Hydrocarbons (PAHs) from traffic sites

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Abstract

Atmospheric PM_{2.5} size particulate-associated Polycyclic Aromatic Hydrocarbons (PAHs) were analyzed from December 2018 to May 2019 over three traffic sites of Chota Nagpur Plateau (CNP) of India were analyzed to study their temporal and seasonal variations. Over the last few decades, CNP becomes a hotspot of air pollution due to traffic and anthropogenic activities. The PM_{2.5} concentration was higher than the value given by the National Ambient Air Quality (NAAQ) standard value. The results show the total average concentration of PAHs was found 141.48±22.86, 163.80 ±30.43, and 171.60±26.23 ng/m³ over site (Adityapur) ADP, (Sakchi) SKI, and Mango (MGO), respectively. The PM_{2.5} total average concentration was found 67.91± 14.04, 79.70± 13.53, and 103.20± 21.77µg/m³ over site ADP, SKI, and MGO, respectively. Diagnostic ratio analysis reveals that the source of PM_{2.5} associated with PAHs was petrogenic, pyrogenic, coal combustion, and vehicular emission. Backward trajectories model and fire count data were also used for air parcel movement up to height 4500 m above the earth's surface. The traffic campaign has provided a rare opportunity for the CNP region for the collection of more air pollution baseline data, which could be helpful in the formulation of air pollution reduction policies in the future

1. Introduction

Last few decades, air pollution becomes a major problem on the global platform. Particulate matter size less than 2.5 µm (PM_{2.5}) linked Polycyclic Aromatic Hydrocarbons (PAHs) becomes an excessive danger to human health as a consequence of its teratogenic, mutagenic, and carcinogenic properties (Kumar et al., 2020a). Due to the smaller particulate size, it cannot be trapped by the upper part of the respiratory tract and can penetrate the lungs (Thomas, 2013). Particulate having great adsorbing ability by providing a large surface area, where various toxic substances can deposit, including PAHs (Jermann et al., 1989).

PAHs are persistent carbon-based combinations poised of two or additional aromatic rings fused (Yang et al., 2010; International Agency for Research on Cancer (IARC), 1984, 1983; Boeuf et al., 2016; Kumar et al., 2020a). Based on molecular weight, PAHs categories into two classes, Low molecular weight PAHs including two-three rings fused, exist in the vaporous stage, and high molecular weight PAHs, including over four aromatic rings, occur in the particulate stage (Chrysikou and Samara 2009; Baek et al., 1991). United States of Environmental Protection Agency (USEPA) recorded sixteen PAHs as significance pollutant and among them 7 PAHs including chrysene (Chry), benzo[b]fluoranthene (B[b]F), benzo[a]anthracene (B[a]A), indeno[1, 2,3-c,d]pyrene (I[cd]P), benzo[a]pyrene (B[a]P), dibenz[a,h]anthracene (D [ah]A), and benzo[k] fluoranthene (B[k]F) have been categorized as feasible triggering of B2 course human carcinogens (USEPA., 2006).

In emerging countries like India, It is essential to identify air pollution due to traffic emissions. High highway traffic flow is one of the most significant homes of particulate-associated PAHs emission (Yin et al., 2010). The particulate bound PAHs in traffic emission source including, diesel and gasoline exhaust, fuel evaporation, brake pads wear and disc brake, spillage of fuel and lube oil, drains and road outward materials, re-suspension of highway dust, separating, abridgment (Lawrence et al., 2013; Boonyatumanond et al., 2007). Previous studies reported that the motor vehicle contributing 46-90% of

particulate-bound PAH emissions in the urban atmosphere (Jang et al., 2013). Apart from these coals, wood, and biomass burning, industrial emission, like anthropogenic activities, are also responsible for particulate-bound PAHs in the traffic zone (Zhang et al., 2008). Long-distance transport is also accountable for particulate-bound PAHs in the traffic zone (Ravindra et al., 2008). Anthropogenic activities are responsible for particulate emission. Biological activities, including forest fire and volcanic eruption, are also accountable for particulate-bound PAHs in the atmosphere (Kumar et al., 2020a; Xu et al., 2006; Baek et al., 1991).

Jamshedpur is an economic megacity in the Chota Nagpur Plateau (CNP) region provoked by heavy air effluence (Kumar et al., 2020b). The present study, identify of PAH were conducted from December 2018 to May 2019. The samples were collected by mini volume sampler to assess PM_{2.5} bound PAH concentrations temporal deviations and understand probable source ranges of PAH using diagnostic ratio (DR) models. Furthermore, we also consider the spatial and periodic features of PM_{2.5} associated PAHs. These study potential implications will be to make a more robust air quality management plan of the city and recognize source-specific effects of particulate matter on human health. The key objective was to expand better empathetic compound characteristics, seasonal disparity, probable causes, and human health hazard calculation due to particulate bound PAHs at Jamshedpur city traffic area.

2. Materials And Methods

2.1 Study area

Measurements of PM_{2.5} bound PAHs have been performed over three sites Adityapur (ADP), Mango (MGO), and Sakchi (SKI). The site selection was made in such a way that to cover the overall scenario and the small-vehicle, significant vehicle movement during the study area (Figure 1). The traffic site is located in Jamshedpur city, the central region of CNP India longitude and latitude (22° 80' N and 86° 20' E). This town is bordered by luxurious green Dalma peaks covering 209 km² at the Chota Nagpur Plateau (CNP). There are tropical dry and wet weather and climate over this study area. Conferring to the registration of 2011, Jamshedpur whole habitat is about 1.3 million, with 6400 persons per km² density of populace (Census 2011). Total 8 33,983 registered vehicles are running in Jamshedpur, East Singhbhum district of Jharkhand state of India (<https://vahan.parivahan.gov.in>). Jamshedpur is one of the decent organized and biggest industrial Cities of CNP. More than one thousand industries are running under the Adityapur Industrial Development Authority (AIDA). Due to many industries such as chemical plants, paint industry, steel industry, plastic industry, etc., emission of large amounts of air pollutants. The transportation of goods and industrial products to other states leads to a high load on Jamshedpur traffic. Traffic emission is also responsible for the PAHs emission in the environment.

2.2 Sampling procedure

The ambient PM_{2.5} sample monitoring was performed from selected locations in CNP on the seasonal event. A total of 48 samples were collected throughout the winter and summer from December 2018- May

2019. The sampling was done by a mini volume sampler (Envirotech Model type APM 550) functioning at a flow rate of 16.5 L/m³. During the campaign 47 mm PTFE filter (Merck, Catalog no- PM2547050) was used to accumulate particulate-phase PAHs. Pre-digested filters were weighed thrice to get accurate weight before sampling. Loaded filter with particulate matter are also weighed thrice after sampling to decide the exact mass of the particulate by a lone pan-top packing numerical weight machine (VWR, Model no: VWR1611-2263: with Weighing chamber L×W×H: 162×171×225 mm). Background impurity was checked by expending functioning blanks (unexposed filters) treated concurrently with field samples. Furthermore, the filter is kept in aluminum foil and packed well, and preserved in a culture box. Before the investigation, these samples were retained in a fridge at under 4⁰C for conservation.

2.3 Sample analysis

Analysis of filter containing PM_{2.5} associated 16 USEPA Priority PAHs including Naphthelene (NAP), Acenaphthylene (Acy), Chrysene (Chr), Benzo[a]pyrene (BaP), Acenaphthene (Ace), Phenanthrene (Phe), Anthracene (Ant), Benzo[ghi]perylene (B(ghi)P), Fluoranthene (Flua), Pyrene (Pyr), Indeno[123-cd]pyrene (IcP) Fluorene, (Flu), Benzo[a]anthracene (BaA), Benzo[k]fluoranthene (BkF), Benzo[b]fluoranthene (BbF), and Dibenzo[ah]anthracene (DBahA), was performed. The filter paper was cut into smaller pieces. The filter was extracted with 200 ml dichloromethane (DCM) for 20 hours with an identified extent of a standard surrogate solution of Pyrene-D10 (CAS Number -1718-52-1), Anthracene-D10 (CAS Number -1719-06-8), Phenanthrene-D10 (CAS Number -1517-22-2), Naphthalene-D8 (CAS Number -1146-65-2) and Chrysene-D12 (CAS Number -1719-03-5). After that, the extracted solution volume was reduced by the rotatory evaporator. The extracts were purified using sodium sulfate – silica gel column (glass column of 30cm long and 3cm diameter). The target solutions were eluted with 10 ml dichloromethane (DCM) and hexane solvent (1:1v/v). The further purified excerpt was reduced up to 1-2 ml by again rotatory evaporator. The PAHs were recognized by the Gas Chromatography attached by the Flame Ionization Detector (GC- FID, Agilent-7890B) furnished with capillary pillar HP- 5MS (30 m × 0.32 mm × 0.25 μm) with a seven-inch cage. In a split less manner, 1 μl of every sample was inserted. Nitrogen gas was used as a transferor gas with a flow rate of 2 ml min⁻¹. The oven temperature was initiated at 60⁰ C for 3 min and improved up to 320⁰ C at the rate of 5⁰ C min⁻¹ and hold for 20 min. The peak area of individual bands and retention factor, the 16 USEPA significance PAHs concentrations were quantified. Recoveries of PAH complexes were above 75%. The laboratory field test and blanks blank test has performed for samples were revealed and examined in the identical technique as field test sample investigation, and the PAH compound was not perceived in blank samples. The sample and blank solutions were then transferred into 50 mL vials, labeled, and stored in the refrigerator before analysis.

2.4. Quality control

The deuterated labeled PAHs; Pyrene-D10, Anthracene-D10, Phenanthrene-D10, Naphthalene-D8, and Chrysene-D12 were used for the recovery studies, and the recoveries were 98 ± 13%, 82 ± 14%, 92 ± 13%, 38 ± 12%, and 103 ± 12%, respectively. The method detection limits (MDLs) were examined using the laboratory blanks and 8 field blanks spiked with the known number of targeted PAHs standards. The

MDLs were calculated as the mean concentration of target compounds in field blanks in addition to the blanks standard deviation three times. The limit of quantifications (LOQs) was designed as ten times the standard deviation. Field blank analysis was used to eliminate the error during the sampling campaign. The LOD and LOQ value was in the array of 0.01-0.05 and 0.04-0.20 $\mu\text{g/l}$ correspondingly. The concentration was less than the detection limit considered as (<DL).

3. Results And Discussion

3.1 Spatial-temporal variations of $\text{PM}_{2.5}$ associated PAHs

The detail of the seasonal concentration of PAHs and $\text{PM}_{2.5}$ given in Table 1. The total average concentration of PAHs was found 141.48 ± 22.86 , 163.80 ± 30.43 , and 171.60 ± 26.23 ng/m^3 over site ADP, SKI, and MGO, respectively. The $\text{PM}_{2.5}$ total average concentration was found 67.91 ± 14.04 , 79.70 ± 13.53 , and 103.20 ± 21.77 $\mu\text{g/m}^3$ over site ADP, SKI, and MGO, respectively. The concentration of $\text{PM}_{2.5}$ was more significant than the national ambient air quality (NAAQ) standards value of $40 \mu\text{g/m}^3$ (NAAQS, .2009) over the three study sites.

The $\text{PM}_{2.5}$ associated with PAH concentration was recorded higher in the winter season than the summer season over the study site ADP, SKI, and MGO. The PAHs concentration in the winter season was found 160.40 ± 13.34 , 190.70 ± 16.58 , and 194.77 ± 12.30 ng/m^3 over area ADP, SKI, and MGO, respectively. PAHs concentration during the summer season was 122.56 ± 11.13 , 136.90 ± 7.36 , and 148.44 ± 9.81 ng/m^3 at ADP, SKI MGO, respectively. The total average concentration of $\text{PM}_{2.5}$ was found 80.27 ± 6.62 , 90.80 ± 8.46 , and 121.95 ± 8.20 $\mu\text{g/m}^3$ in the winter season and summer season 55.55 ± 5.44 , 68.61 ± 6.28 and 84.45 ± 12.01 $\mu\text{g/m}^3$ over ADP, SKI, and MGO site, respectively. The seasonal concentrations of 16 PAHs are plotted in Figure 2, and the total average concentrations of PAHs and $\text{PM}_{2.5}$ are shown in Figure 3.

Calculated $\text{PM}_{2.5}$ linked PAHs in the winter season was found more remarkable than other seasons because of the primary source of emission, such as domestic cooking or heating emission, vehicular emission, etc. Additionally, the concentration was high because of the reduction of atmospheric dispersion of particulate and PAHs concentration sorption on particulate bound PAHs due to a decrease in air temperature (Ravindra et al., 2008). Furthermore, particulate-bound PAH concentration is generally found less in the warm period because of less emission from primary sources. Metrological conditions like higher temperature and wind allow them to dispersion with higher mixing height, favoring the pollutant in gas phase portioning and photodegradation of $\text{PM}_{2.5}$ associated PAHs. A similar seasonal variation has been designated in earlier work (Chrysikou and Samara, 2009; Gianelle et al., 2013).

3.2 Diagnostic Ratio Analysis

Diagnostic ratios of PAHs were used to deliver reliable evidence on PAH's emission cause in the atmosphere. The ratio of Ant/(Ant+Phe), Flua/(Flua+Pyr), Flua/Pyr, Phen/Ant IcP/(IcP+B(ghi)P), and BaP/B(ghi)P were used to determine the seasonal cause of emission of particulate linked PAHs. The

value of Ant/(Ant+Phe) ratio is less than 0.1 directed petrogenic source and significance upper than the 0.1 indicated pyrogenic source over all the three traffic sites (Pies et al., 2008). The ratio of Flua/(Flua+Pyr) less than 0.1 directed petrogenic/ unburned petroleum source, the value found between 0.4-0.5, the source is fossil fuel burning if value found higher than 0.5 the source identified as coal & biomass burning (Yunker et al., 2002; De La Torre-Roche et al., 2009). The ratio of Flua/Pyr less than 0.1 directed, petrogenic cause, and larger than 1 indicated fossil fuel combustion cause (Sicre et al., 1987). The ratio of Phen/ Ant less than 10 indicated the pyrogenic source, and higher than 10 directed coal combustion was the predominant source. The ratio of BaP/B(ghi)P and Icp/(Icp+B(ghi)P) was an indicator for traffic and non -traffic emission sources of PAHs over all the site (Hussain et al. 2015). The PAHs ratio over three traffic sites ADP, SKI, and MGO, plotted in Figure 4, indicating the petrogenic, Pyrogenic, coal burning, and vehicular discharge was the chief source of emission of PAHs over the study site in both cold and warm seasons of CNP.

3.3 Backward Trajectories

The backward trajectories model was used for improved perception of contamination affected by air particulates transported by air or discharged by the resident basis causes. Proportions of height coordinates with respect 7- day isentropic back trajectory was investigated for full run time 168 h up to altitude level of 500 m with Meteorological Data Explorer (METEX, <http://db.cger.nies.go.jp/metex/trajectory.html>) in winter and summer season as shown in Figure 5. At various heights up to 4500 m beyond the ground, back trajectory analysis has been examined to elucidate aerosol possessions changeability linked with airborne particulate matter in the whole atmospheric outline on a seasonal basis. Winter season trajectories show that most of the Indo- Gangetic plain (IGP) mass is from the central Asia region. Summer season trajectories show that the aerosol mass loading form mainly originated from CNP. Some assembly was loaded from the Bengal region, south and south-Eastern part of the country.

Fire counts data were also incorporated in the backward trajectory model by the Moderate Resolution Imaging Spectroradiometer (MODIS) from the National Aeronautics and Space Administration (NASA) satellite was used to assess dynamic combustion over India during the study period. The unified fire count data are accessible at <https://earthdata.nasa.gov/earth-observation-data/near-real-time/firms>.

3.4 Health Risk Assessment

The adverse effect of the introduction of particulate-linked PAHs on human health is calculated by the equivalent toxicity concentration (TEQ) equation (Yu et al., 2008; Yang et al., 2007). TEQ expression represents the sum of assessed carcinogenic risk qualified to BaP for entirely PAHs having carcinogenic potential, which can be assessed by multiplying the concentration of every PAHs carcinogenic and toxicity equivalence factor (TEF) value given by Nisbet and Lagoy (1992) 1 value for BaP and DBahA, 0.1 value for BaA, BkF and Icp, 0.01 value for Chr, Ant, and B(ghi)P and 0.01 for Phe, Flt, and Pyr for each PAH. The following equation was used to determine the TEQ value.

$$TEQ = \sum C_i \times TEF_i$$

Where C_i and TEF_i represent the concentration of specific PAHs and toxic equivalency factors, respectively. DBahA and BaP contribute the highest carcinogenicity of PAH samples on average. BaP gives 35.72, 38.11, and 39.54 % carcinogenicity over the PAHs samples traffic site, respectively. DBahA contributed 50.52, 47.82, and 45.25 % carcinogenicity over ADP, SKI, and MGO sites, respectively. This confirms the surrogate compounds were DBahA and BaP in evaluating PAHs health threat.

The exposure threat due to individual PAHs can be quantitatively calculated by Incremental lifetime cancer risk (ILCR) (Peng et al., 2011; USEPA., 1991; Chen and Liao., 2006). ILCR was considered by assessing the corresponding lifetime average daily dose (LADD) of PAHs by allowing in two age group, children (age 6 years) and adult (age 70 years), having Inhalation rate (IR) air inhalation rate of 10 m³/day for children and 20 m³/day for an adult (Soltani et al., 2015). The Exposure frequencies (EF) were considered 365 days/year for both children and adults (Kumar et al., 2013). Bodyweight of child and adult were considered 18 kg for child and 60 kg for adults (ICMR., 2009), and the averaging time (AT) for hazards was 70 years. Exposure duration was considered as 24 years (USEPA., 2011). The following equation was used to calculate LADD and ILCR.

$$LADD \text{ (mg kg}^{-1} \text{ day}^{-1}\text{)} = (C_s \times IR \times CF \times EF \times ED) / (BW \times AT)$$

$$ILCR = LADD \times CSF \text{ (Cancer Oral Slope Factor)}$$

C_s is the quantity of PAHs renewed concentration grounded on TEQ assessment in airborne particulate (ng/m³). In the present study, CSF symbolizes the inhalation cancer slope factor (3.85 mg kg⁻¹ day⁻¹) (Peng et al., 2011). The LADD value and ILCR value were calculated, and the values of the details are presented in Table 3. Auxiliary, the Excess Life Time Cancer Risk (ELCR) was assessed by the sum of ILCR for Adult and ILCR value for the child overall study site. The ELCR value over ADP, SKI, and MGO sites was found 13.89×10^{-6} , 16.17×10^{-6} , and 16.49×10^{-6} respectively. The ELCR value lies in the tolerable limit 10^{-6} - 10^{-4} given by USEPA (USEPA. 1989). The outcome presented that the risk level was tolerable over ADP, SKI, and MGO traffic sites.

3.5 Conclusion

In the present study, PM_{2.5} associated PAHs were examined in three CNP traffic sites in the cold and warm seasons. The total average concentration of PAHs was found 141.48 ± 22.86 , 163.80 ± 30.43 , and 171.60 ± 26.23 ng/m³ over area ADP, SKI, and MGO, respectively. The PM_{2.5} total average concentration was found 67.91 ± 14.04 , 79.70 ± 13.53 , and 103.20 ± 21.77 μg/m³ over site ADP, SKI, and MGO, respectively. The concentration of PM_{2.5} was found upper than the NAAQ standards value of 40 μg/m³ over the three study sites in together (cold and warm) season. The concentration of PM_{2.5} linked PAHs was found upper in the cold season than the warm season. Diagnostic ratio analysis reveals that the source of PM_{2.5} allied PAHs was petrogenic, pyrogenic, coal combustion, and vehicular emission was the

principal cause of emission of PAHs. Backward trajectories model and fire count data were also used for air parcel movement up to height 4500 m above the earth's surface. The health threat due to the introduction of PM_{2.5} linked PAHs was analyzed. BaP and DBahA were the highest contributors to carcinogenicity. BaP contributes 35.72, 38.11, and 39.54 % carcinogenicity over the PAHs samples traffic site, respectively. DBahA contributed 50.52, 47.82, and 45.25 % carcinogenicity over ADP, SKI, and MGO sites, respectively. LADD and ILCR value was also calculated for all the study site. The ELCR value over ADP, SKI, and MGO site was found 13.89×10^{-6} , 16.17×10^{-6} , and 16.49×10^{-6} , respectively. The obtained data represent an exclusive contribution to the complex assessment of human exposure to PAHs in traffic sites, with the background of mid and heavy traffic zones.

Declarations

Acknowledgments

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Compliance with Ethical Standards Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Tables

Due to technical limitations the Tables are available as a download in the Supplemental Files.

Figures



Figure 1

Three traffic sampling site of Adityapur (ADP), Sakchi (SKI), and Manno (MGO) area of East India. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

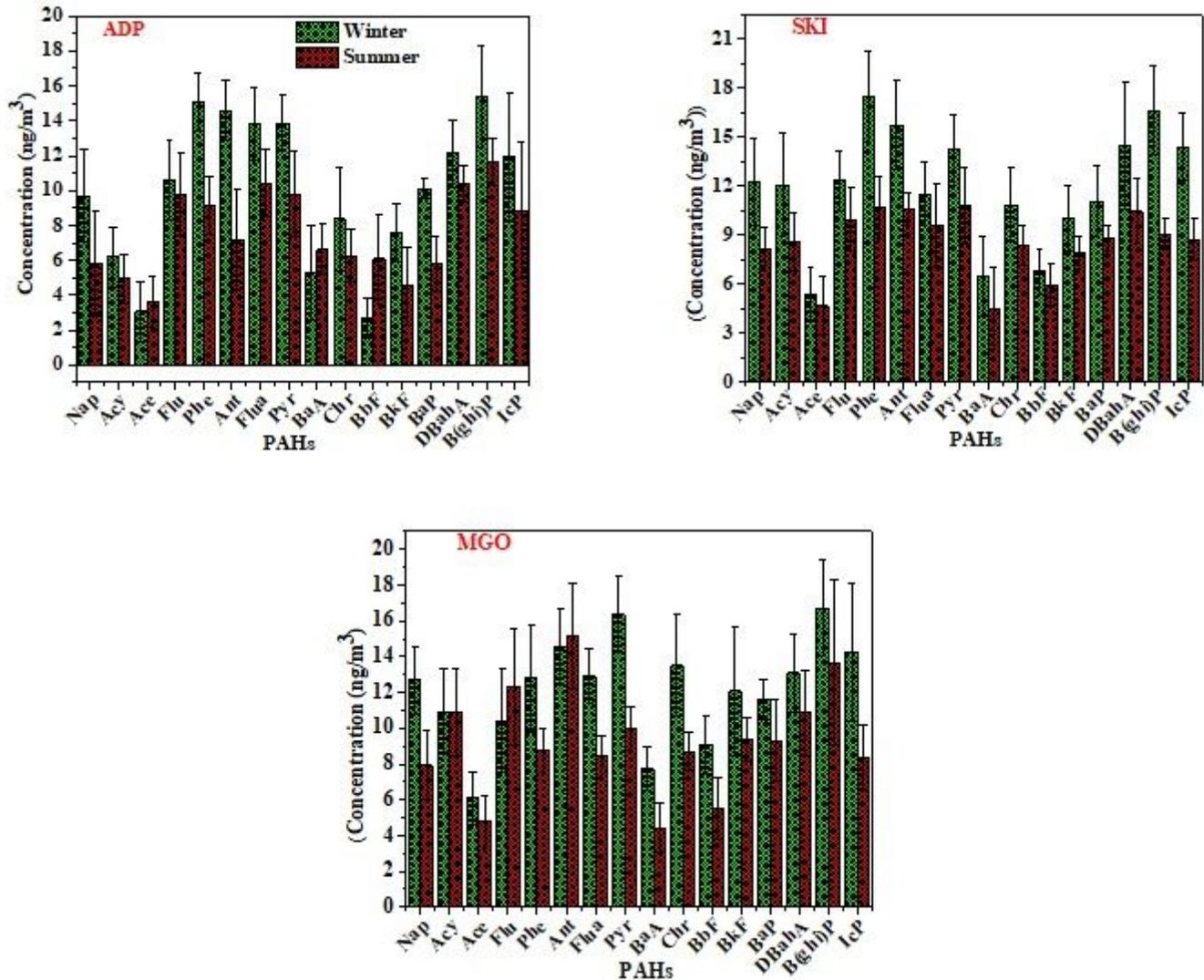


Figure 2

Concentration of PAHs in three traffic sites of Adityapur (ADP), Sakchi (SKI), and Manno (MGO) area.

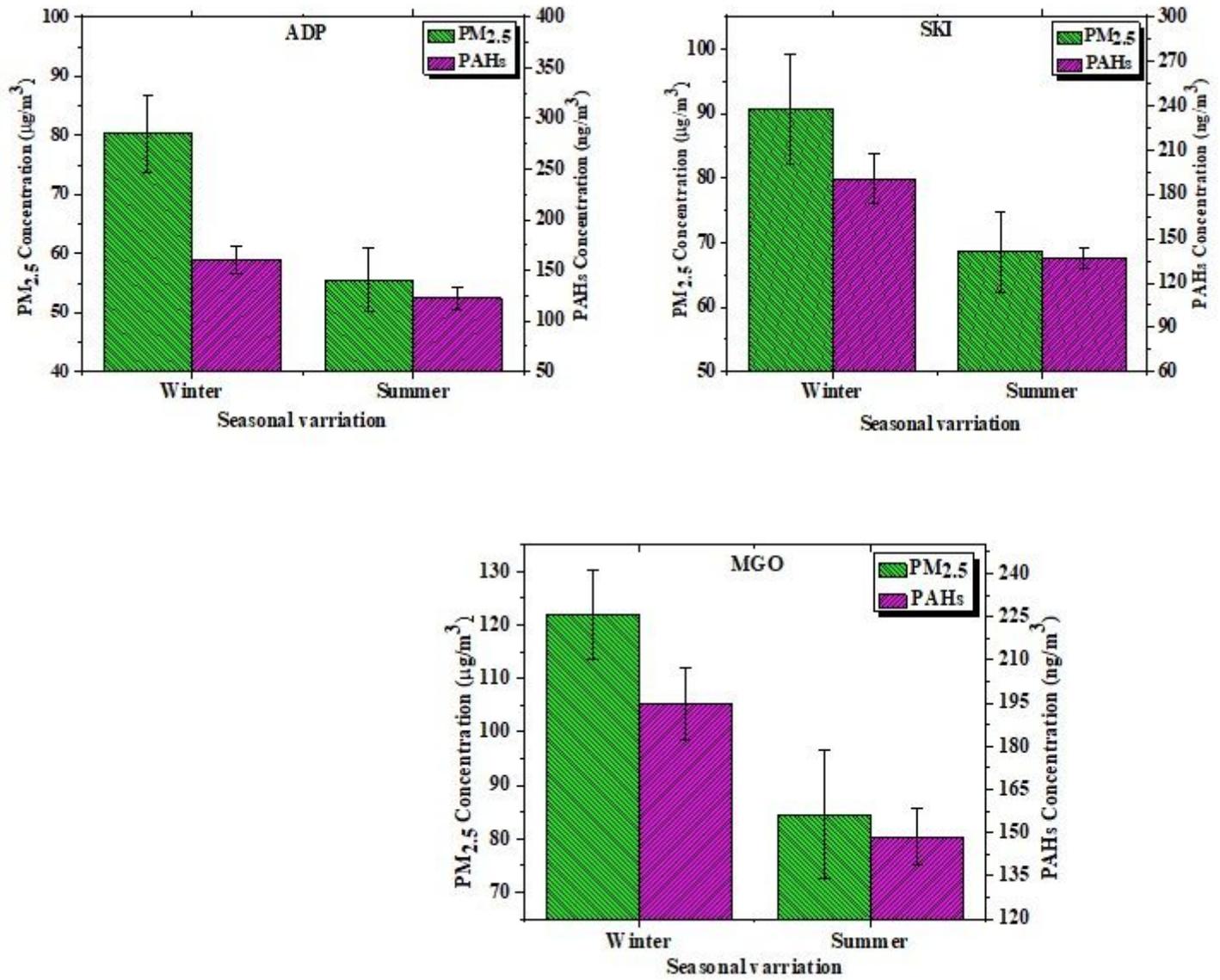


Figure 3

Seasonal concentration of PM_{2.5} (µg/m³) and PAHs (ng/m³) over three CNP traffic sites.

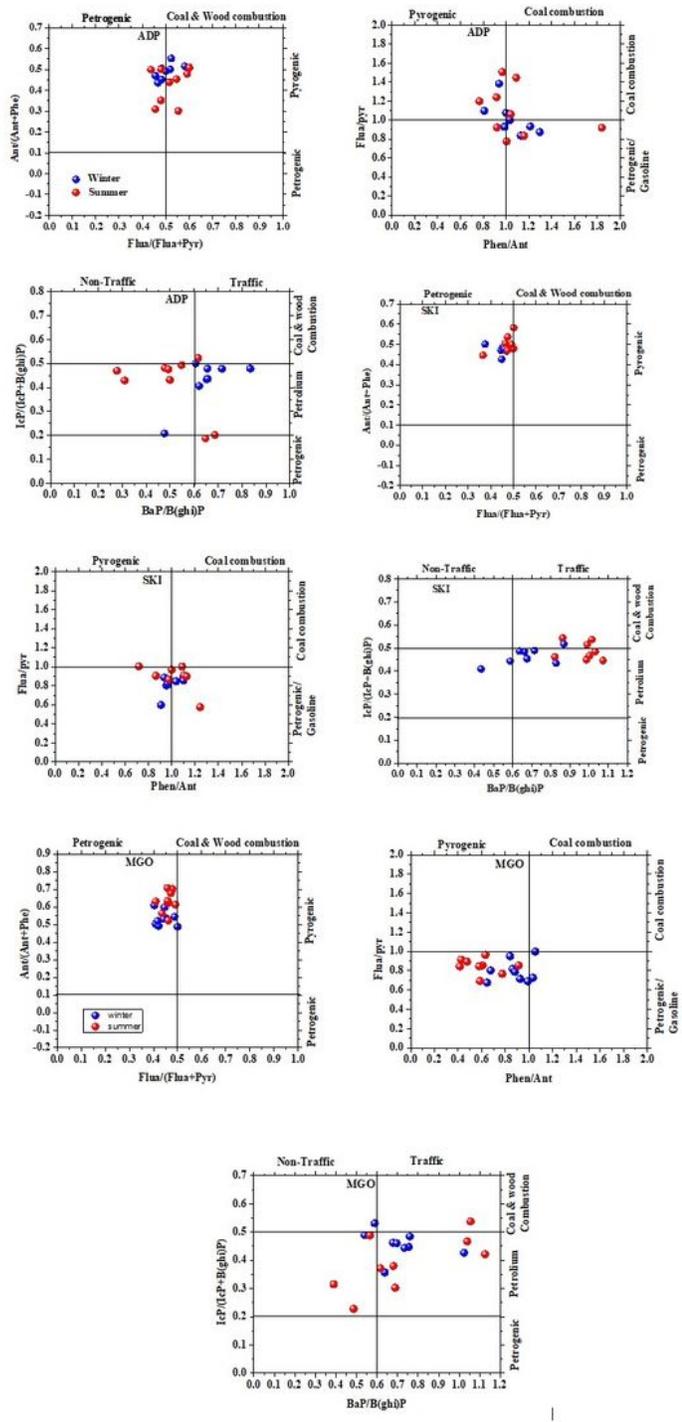


Figure 4

Diagnostic Ratio analysis for source apportionment over three sites ADP, SKI & MGO of CNP.

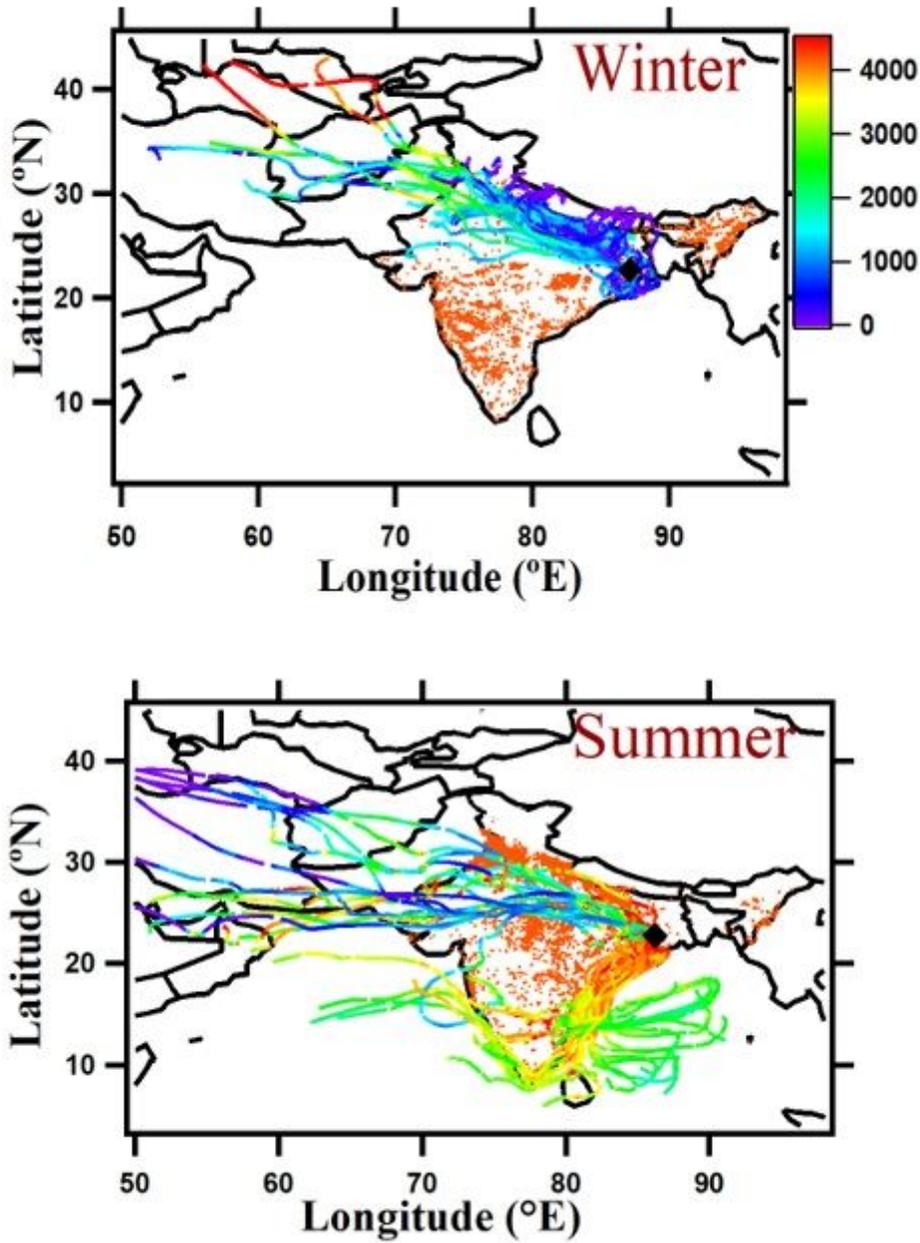


Figure 5

7 Days Backward trajectories up to 500m from the surface and fire count data of East India (Latitude- 22.80460N, Longitude- 86.2029 0E)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Table.pdf](#)