



Distribution of Gaseous Phase Polycyclic Aromatic Hydrocarbons (PAHs) in Rural Environment of India

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Abstract

Polycyclic aromatic hydrocarbons are considered as atmospheric contaminants due to their carcinogenic and mutagenic properties. In the present study, 8 selected gaseous phase PAHs were determined in ambient air representing rural environment. The gaseous phase PAHs samples were investigated for quantification of selected PAHs in various seasons and possible sources of gaseous phase PAHs in rural environment. The samples were collected using a cartridge containing XAD-2 resin placed between layers of polyurethane foam (PUF) and analyzed by fluorescence technique. The seasonal variation in selected gaseous phase individual PAHs varied between 28-496.9 ng m⁻³ during winter, summer and post-monsoon season respectively. The concentration of gaseous phase PAHs was dominated by Phen, Anth and Flt. The gaseous phase concentration of PAHs were 3.9 and 5.1 times higher in winter as compared to summer and post-monsoon season respectively. The higher concentration winter may be due to higher emission from biomass burning, fuel used for cooking such as coal and kerosene and other heating activities to protect from cold winter. The three ring gaseous phase PAHs were predominant than four and five membered ring PAHs and contribution varied between 74.9-93.9 % of selected PAHs. The ratio analysis studies showed that traditional fuel used for cooking purposes mainly wood, kerosene, coal and biomass burning are the major contributors in rural environment.

Keywords: Polyurethane foam (PUF), seasonal variations, gaseous phase PAHs.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are multi ringed compounds and have received considerable attention because of their potent carcinogenic and mutagenic nature^{1,2}. Their characteristics of lipophilicity, low water solubility and adsorption to aerosol particles makes them dangerous threat to the different component of environment as these PAHs compound may undergo chemical transformation reactions, causing damaging effects on human health and its environment. PAHs are derived from anthropogenic sources and are products of incomplete combustion process. Anthropogenic sources in addition to natural sources may also contribute significantly to the concentration of PAHs in the environment³. These PAHs decompose under strong solar radiation, undergo thermal decomposition and react with other pollutants to produce more toxic derivative compounds⁴.

PAHs exists in particulate and gaseous phases. The particulate phase PAHs are more carcinogenic in nature as compared to gaseous phase PAHs in ambient air. Depending on their molecular weights and vapor pressure, 3 membered ring concentrations are higher and 4 and 5 membered ring concentration are lower in gaseous phase PAHs. Industrial activities, automotive vehicle exhaust, domestic cooking fuels are the main sources of PAHs but it is very difficult to identify the sources of PAHs from petrogenic or pyrogenic. The physical

and chemical properties of PAHs like chemical reactivity can modify the original distribution pattern of emission sources⁵⁻⁸. The main aim of this study is to characterize the selected gaseous phase PAHs concentration, seasonal variations and possible sources to better understand the sources of PAHs and their transformation mechanism in the atmosphere of rural environment.

Material and Methods

Study Area: The Akkalkuwa, Nandurbar, Maharashtra is located in Satpuda range of hills. This is typical Indian rural area of a semi-arid region in North western side of the State. The area has hilly terrain and falls in forest area. The area of Akkalkuwa is spread about 878 sq.km with population of 17737. Nandurbar District is generally hot and dry. Temperatures can be as high as 45°C during the peak of Summer and 11°C in winter season. The average rainfall in the village is 859 mm. The rapid urbanization has resulted in the increased utilization of fuels for transportation and wood for domestic purposes. Type of fuel used for cooking in homes, the type of fuel used in vehicles are all important parameters that influences the PAH concentration in any area.

Gaseous Phase Sampling and Analysis: Aerosols sample was collected from Akkalkuwa Station (21°33'5"N and 74°01'17.2"E) on 24 hrs basis using pre-weighted quartz fibres

representing winter (December-January-February), summer (March-April-May) and post-monsoon (September-October-November) season are published elsewhere⁹. Samples was collected at a flow rate (1.1-1.3 m³/min) using particulate samplers (APM-460 Envirotech India) at 3 m above the ground level. After particle collection, the exposed filters were stored in a freezer to limit losses of volatile components. Similarly, the gas phase compounds were collected using a cartridge containing XAD-2 resin placed between layers of polyurethane foam (PUF). The gaseous phase PAHs adsorbed on PUF were cleaned by sonication applying 5 ml dichloromethane (DCM) in a 15 ml glass vial. The sonication was done for 15 min in ultra-sonication. The process of ultra-sonication was treated using 5 ml methanol for the same used filter paper in the same vials. This process was done for all samples. The vial was left overnight. The white crystalline content obtained in the glass vial was dissolved by adding 5 ml acetonitrile and agitated in water bath for 3 hours at 70 rpm, later the glass vial was centrifuged and supernatant was collected and analyzed. The supernatant collected was put for analysis by fluorescence spectrophotometer. Model F-4500, Hitachi Japan, was used for PAHs quantification reported elsewhere. And the system has optimized for software and hardware in the widest range of fluorescence applications⁹. In this technique of analysis, the excited light source is commonly a xenon arc lamp which has an intense emission spectrum from 200-900 nm, which is capable to excite molecules using both ultraviolet and visible wavelength ranges. The emission fluorescence is detected by a photomultiplier tube (PMT) positioned at a 90° angle from the incident light path. The PAHs analyzed in aerosols were Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Pyrene (Pyr), Chrysene (Chr), Anthracene (Anth), Benzo(a)pyrene (BaP) and Fluoranthene (Flt) at an experimental wavelength of 306, 313, 364, 385, 393.6, 407, 431, 454.3 nm respectively.

The fluorescence spectrophotometer was calibrated by using PAHs mix standards (Accu Standard, AE-00025, New Haven, CT). It contained 8 analytes in acetonitrile. Three levels of concentrations were made from the standard PAHs mix in the concentration range 2.5, 5 and 10 parts per billion (ppb). Identification of peak was done on the basis of wavelength. Each level of PAHs standard was analyzed and intensity was obtained from the axes of wavelength versus intensity. Peak intensity was calculated at the experimental wavelength versus intensity peak. The concentration of all fluorescent PAHs was determined in air particulate samples using following expression.

$$\text{Conc. of PAHs} = \frac{\text{Peak intensity of individual sample}}{\text{Peak intensity of std.}} \times \text{Conc. of calc. PAH} \quad (1)$$

Quality Control and Data Analysis: During the analysis, known amount of standard mixtures were spiked onto blank PUF to ensure Quality Control (QC). In all 8 unknown samples, two PUF blanks and 2 PUF QC samples were taken for analysis. Also an external recovery standard and calibration standards were also analyzed in parallel along with sample extracts. The external recovery standard included all the eight PAHs. In addition the following steps were followed to ensure complete QC during the course of analysis and sample measurements may not fall above or below 2 standard. Further quality assurance was ensured by conductivity and drift check. Fluorescence intensities were recorded for de-ionized, distilled water at 277 nm EX/303 nm EM to assure consistent measurements between analyses. Similarly, wavelength accuracy checks were also made four times to assure consistent emission from the xenon lamp. The parameters were set (according to software guidelines) to analyze a standard diffusion parameters¹⁰.

Results and Discussion

Seasonal Variations in Gaseous Phase PAHs Concentration:

The seasonal variation in selected gaseous phase individual PAHs measured are presented in table 1. During winter season, the concentration of total PAHs varied between 157.2-496.9 ng m⁻³ with an average concentration of 255 ng m⁻³. The concentration of gaseous PAHs measured was found in the range of 12.6-75.5 ng m⁻³ for Flt, 4.4-43 ng m⁻³ for Pyr, 45.2-168.4 ng m⁻³ for Phen, 5.6-24.5 ng m⁻³ for Ace, 0.6-2.6 ng m⁻³ for Chr, 11.3-114.3 ng m⁻³ for Anth, 0.2-0.5 ng m⁻³ for BaP and 12.7-78.5 ng m⁻³ for Flu. The concentration of individual gaseous phase PAHs in the decreasing order as Phen>Anth>Flu>Flt>Pyr>Ace>Chr>BaP. During summer season, the concentration of total PAHs varied between 36.8-105.3 ng m⁻³ with an average concentration of 67.6 ng m⁻³. The concentration of gaseous PAHs measured was found in the range of 1.6-9.5 ng m⁻³ for Flt, 0.2-1.6 ng m⁻³ for Pyr, 23.8-88.9 ng m⁻³ for Phen, 0.5-2.4 ng m⁻³ for Ace, 0.1-0.3 ng m⁻³ for Chr, 2-16 ng m⁻³ for Anth, 0.1-0.2 ng m⁻³ for BaP and 1.1-6.9 ng m⁻³ for Flu. The concentration of individual gaseous phase PAHs in the decreasing order as Phen>Anth>Flu>Flt>Ace>Pre>Chr>BaP. During post-monsoon season, the concentration of total PAHs varied between 28-78.8 ng m⁻³ with an average concentration of 50.9 ng m⁻³. The concentration of gaseous PAHs measured was found in the range of 1.1-6.8 ng m⁻³ for Flt, 0.1-1.3 ng m⁻³ for Pyr, 16.8-62.7 ng m⁻³ for Phen, 0.3-1.4 ng m⁻³ for Ace, 0.1-0.3 ng m⁻³ for Chr, 2.6-18.2 ng m⁻³ for Anth, 0.1-0.2 ng m⁻³ for BaP and 0.7-4.2 ng m⁻³ for Flu. The concentration of individual gaseous phase PAHs in the decreasing order as Phen>Anth>Flt>Flu>Ace>Pyr>Chr=BaP. The concentration Phen, Anth and Flt was highest among all selected PAHs. These are low molecular weight PAHs which tend to exist in gaseous phase and are the products of incomplete combustion and pyrolysis of fuels¹¹.

Table-1
Seasonal Variation in Gaseous Phase PAHs(ng m^{-3}) at Akkalkuwa

PAHs	Ace	Flu	Phen	Pyr	Chr	Anth	BaP	Flt	Total PAHs
Mol wt.	154	166	178	202	228	178	252	202	
rings	3	4	3	4	4	3	5	3	
Winter	13.7±4 (5.6-24.5)	42.8± 15.8 (12.7-78.5)	90± 35 (45.2- 168.4)	19.4± 8.5 (4.4-43)	1.1± 0.5 (0.6-2.6)	48.6± 26.2 (13.8-114.3)	0.3± 0.1 (0.2-0.5)	25.6± 12.8 (12.6-75.5)	260± 65 (157.2- 496.9)
%	5.2	16.9	37.3	7.6	0.5	21.7	0.1	10.7	-
Summer	1.3±0.4 (0.5-2.4)	3.8± 1.4 (1.1-6.9)	49.8± 18.5 (23.8-88.9)	0.8± 0.3 (0.2-1.6)	0.2± 0.1 (0.1-0.3)	7.7± 3.6 (2.0-16)	0.2±0 (0.1- 0.2)	3.4± 1.6 (1.6-9.5)	67± 18.3 (36.8-105.3)
%	1.9	5.7	74.3	1.1	0.2	11.4	0.2	5.1	-
Post- monsoon	0.7± 0.2 (0.3-1.4)	2.3± 0.9 (0.7-4.2)	35.3± 13.1 (16.8-62.7)	0.6± 0.3 (0.1-1.3)	0.1± 0.1 (0.1-0.3)	9.4± 4.3 (2.6-18.2)	0.1± 0 (0.1-0.2)	2.4± 1.2 (1.1-6.8)	51± 12.8 (28.-78.8)
%	1.4	4.5	69.2	1.1	0.2	18.5	0.2	4.8	-

Comparison with seasonal pattern: The ratio of winter to summer and winter to post-monsoon was observed as 3.9 and 5.1 times higher in winter. The high concentration of gaseous phase PAHs depends upon atmospheric conditions. In winter, slow wind speed and low temperature decreases the dispersion of pollutants which contributed to build up of pollutants in the atmosphere. Further, high concentration may also be due to higher emission from biomass burning, fuel used for cooking such as coal and kerosene and other heating activities to protect from cold winter. In summer, due to fast wind speed and hot temperature, dispersion of pollutants increased which leads to decrease in concentration of PAHs in the environment. In post-monsoon season, removal of gaseous PAHs due to wash out effect of precipitation in monsoon causes decrease in gaseous concentration of PAHs in atmosphere¹¹.

Distribution of Gaseous PAHs as per Benzene rings: The abundance and types of PAHs exhibits seasonal variations in gaseous phase. As a thumb rule, 2-3 membered ringed are mainly occur in gas phase, while 5-6 membered ring are adsorbed on aerosols and 4 membered ring tends to occurs in both gaseous and particulate phase. Moreover, gaseous phase PAHs are more sensitive to UV light and they undergo photo-oxidation caused by sunlight in the atmosphere. This process is faster in gaseous phase than particulate phase. The gaseous phase PAHs were categorized according to distribution of ring structure¹². The % contribution of gaseous PAHs during winter, summer and post-monsoon season are presented in Figure-1. During winter season, the 3 membered ring contributed 74.5%, 4 membered ring 25% and 5 membered ring 0.1%. The highest

contribution of 3 membered ring may due to its tendency to exist in gaseous phase because of low molecular weight and vapor pressure. The 4 membered ring has tendency to exist in gaseous as well as particulate phase and 5 membered ring has insignificant contribution in gaseous phase. During summer season, the 3 membered ring contributed 92.7%, 4 membered ring 7% and 5 membered ring 0.3%. During post-monsoon season, the 3 membered ring contributed 93.9%, 4 membered ring 5.8% and 5 membered ring 0.3%. Among the selected PAHs, Phen, Anth, Flu and Flt are the most abundant PAHs during winter, summer and post-monsoon season respectively. The gaseous phases PAHs are typical tracers of primary emissions from biomass burning, domestic heating, kerosene fuel used for domestic purposes which is a tradition in rural environment.

Comparison of Gaseous Phase PAHs with other cities: The comparison between concentrations of gaseous PAHs observed during winter, summer and post-monsoon season in Akkalkuwa and other studies reported at other sites are presented in table-2. The average concentration of selected PAHs in the present study was observed as 260, 57 and 61 ng m^{-3} during winter, summer and post-monsoon season respectively. The concentration of PAHs at Hong Kong was higher than present study during winter and summer season⁴. Similarly, the reported concentration of PAHs at Hanoi, Vietnam was also higher during winter season¹³. As compared to present study, the gaseous concentration of PAHs at Serbia was lower during winter season¹⁴.

Table-2
Comparison of gaseous phase PAHs with other locations

Locations	Winter	Summer	Post-monsoon	Reference
Hong Kong	1762	1610	-	[4]
Hanoi, Vietnam	400	-	-	[13]
Serbia	201	224	-	[14]
Akkalkuwa	260	57	61	Present study

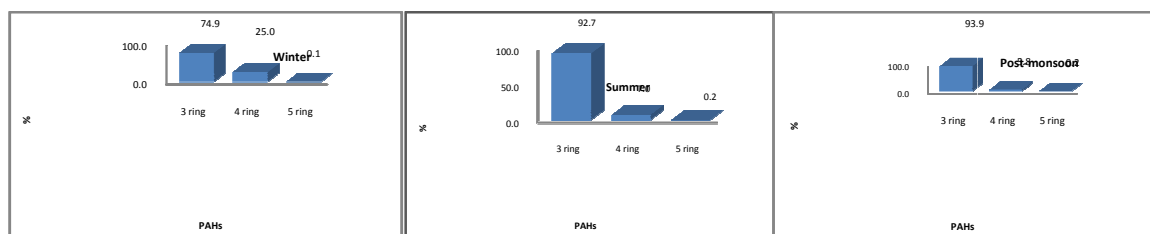


Figure-1
% Contribution of Gaseous PAHs during winter, summer and Post-monsoon season

Diagnostic ratio of gaseous Phase PAHs: Diagnostic ratio has been used to identify the origin of PAHs sources in the atmosphere. An attempt has been made to assess the diagnostic ratio in gaseous phase and is presented in table 2. The Pyr/BaP ratio was 63, 4.52 and 5.17 during winter, summer and post-monsoon season are >0.10 indicates gasoline sources ex. Kerosene used for domestic purposes. The ratio of Flt/(Flt + Pyr) was 0.58, 0.82 and 0.81 during winter, summer and post-monsoon season are >0.5 indicates coal, wood and biomass burning sources. The ratios of Anth/(Anth + Phen) was 0.37, 0.13 and 0.21 during winter, summer and post-monsoon season are >0.1 values indicates coal combustion sources which is used as a cooking medium in rural environment. The ratio of Flu/(Flu + Pyr) was 0.69, 0.83 and 0.80 during winter, summer and post-monsoon season respectively. The values are >0.5 indicates biomass, wood and coal combustion sources in rural environment. Taking into account the entire described diagnostic ratio pointed out that dominant sources were biomass burning, kerosene, coal combustion in rural environment¹⁴.

Conclusions

The PAHs concentrations of gaseous pollutants in rural environment were during winter, summer and post-monsoon season. Their seasonal variation in concentration of gaseous PAHs was characterized. The concentration of gaseous phase PAHs (Phen, Anth and Flt) was highest in winter implies that seasonal variations of individual PAHs species can vary depend on molecular size, volatility and emission sources. Further gaseous phase PAHs are low molecular weight and has tendency to exist in gaseous phase and are also the products of incomplete combustion and pyrolysis of fuels. The three membered ring were predominant in gaseous phase PAHs in all the seasons. The ratio of winter to summer and winter to post-monsoon was observed as 3.9 and 5.1 times higher in winter.

The diagnostic ratios were calculated to estimate the possible sources and types of PAHs that exists in atmosphere. The results showed that biomass burning, kerosene, coal combustion sources were predominant in rural environment.

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Table-3
Characteristics Diagnostic Ratios of PAHs attributed to Specific Sources

Diagnostic ratios	Winter	Summer	Post-monsoon	Values	Possible sources
Pyr/BaP	63	4.52	5.17	0.1	Gasoline
Flt/(Flt+Pyr)	0.58	0.82	0.81	<0.5 >0.5	Gasoline Coal/wood
Anth/(Anth+Phen)	0.37	0.13	0.21	≈0.1	Coal/ Gasoline
Flu/(Flu+Pyr)	0.69	0.83	0.80	<0.4 0.4-0.5 >0.5	Petrogenic Fossil fuel Grass/wood coal combustion

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