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Assessment of Potential Toxic Fraction in Atmospheric Aerosols in Rural Environment

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Abstract

Polycyclic aromatic hydrocarbon (PAHs) has been recognized as carcinogenic and mutagenic environmental pollutants in the atmosphere. They are the products of incomplete combustion of fossil fuels such as petroleum, coal and other organic materials from natural and anthropogenic sources in the rural and urban atmosphere. Eight PAHs were determined in PM_{10} collected at rural environment using Respirable sampler during winter, summer and post-monsoon seasons. The filters were extracted in ultrasonic bath with dichloromethane and analyzed by fluorescence technique. The total PAHs concentration varied from 2.67-17, 2.51-3.79 and 1.63-3.59 ng m^{-3} during winter, summer and post-monsoon season respectively. The benzo(a)pyrene and chrysene were found to be associated with particulate during all the seasons. The diagnostic ratio suggest that PAHs emissions were predominantly associated with coal, wood and biomass burning in rural environment. The higher toxic fraction observed during summer (53.8%) are probable human carcinogens associated with aerosols. Toxic equivalency factor (TEFs) of BaP estimated and expressed as BaPeq was low in concentration. The study could be of great significance for the planners while considering the environmental remedial measures.

Keywords: BaPeq, diagnostic ratio, fluorescence, PAHs, toxic fraction.

Introduction

A parameter of concern, polycyclic aromatic hydrocarbons (PAHs) widely distributed in the environment area multi-ringed organic compounds generated by incomplete combustion of organic materials viz. from biomass and coal burning, petrol and diesel exhaust etc. It is not unusual phenomenon in the Indian context especially in the rural environment where biomass burning is the major source of cooking medium. Open burning is often used as a rapid and inexpensive method for disposing crops or biomass residues, releasing nutrients for the next growing cycle and cleaning land, especially in agricultural field but very often this actually cause severe air pollution problems in many countries[1,2].

The characterization of PAHs emitted from different biomass burning well documented worldwide. The presence of PAHs in air could pose possible health risk to the people due to its mutagenicity and carcinogenicity, therefore stringent regulations on PAHs emission is the need of the day. The characterization of aerosols is important for understanding the contribution of coal, wood and biomass burning emissions and atmospheric chemistry in association with it, in addition to the health risk associated to aerosols[3-7]. The main aim of this study is to assess the diagnostic ratio of various PAHs, estimate the potential toxic fraction and benzo(a) pyene equivalency (BaPeq) concentration in rural environment during winter, summer and post-monsoon seasons.

Material and Methods

Study Area: The Akkalkuwa, Nandurbar, Maharashtra is located in Satpuda range of hills. The river Narmada is on the northern side of the village. This is typical Indian rural area of a semi-arid region in North western side of the State. The area was hilly terrain and falls in forest area. The area of Akkalkuwa is spread about 878 sq.km with population of 17737. Traditional agriculture is the main occupation of farmers and have unique crop diversity which includes maize, sorghum, minor millets and pulses. Nandurbar District is generally hot and dry. Temperatures can be as high as 45°C during the peak of Summer and 11^0C 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.

Aerosol Sampling and Analysis: Aerosols sample was collected from Akkalkuwa Station ($21^0$33’5”N and $74^0$01’17.2”E) on 24 hrsbasis using pre-weighted quartz fibres during November 2009-October 2010 representing winter (December-January-February), summer (March-April-May) and post-monsoon (September-October-November) season. Samples was collected at a flow rate (1.1-1.3 m^3/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.

The fraction of filters trapped with particulate matter 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[8]. The system has optimized for software and hardware in the widest range of fluorescence applications. The principle of fluorescence emission is a type of photoluminescence in which a molecule is promoted to an electronically excited state by adsorption of ultraviolent visible near infrared radiation. Then, 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 are Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Pyrene (Pyr), Chrysene (Chr), Anthracene (Anth), Benzo(a) pyrene (BaP) and Fluaranthene (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 Heaven, CT). It contained 8 analyted 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.

$$\text{Conc. of PAHs} = \frac{\begin{array}{c}\text{Peak intensity of}\\ \text{individual sample}\end{array}}{\text{Peak intensity of std.}} \text{ x conc. of calc. PAHs} \qquad (1)$$

Quality Control and Data Analysis: During the analysis, known amount of standard mixtures were spiked onto blank filters to ensure Quality Control (QC). In all 8 unknown sample, two filter blanks and 2 filter 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. These includes the measurement of the target analytes in the QC sample measurements which 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 be made four times to assure consistent emission from the xenon lamp. The parameters were set (according to software guidelines) to analyze a standard diffusion parameters.

Potential Toxic Fraction of Total PAHs determination: Based on PAHs profile, the toxicity fraction of the aerosols were determined. The formula used for calculation is as follows:

$$\text{Potential Toxic Fraction} = \frac{\text{Conc. of total PAHs}}{\text{Conc. of BaP} + \text{Chr}} \text{ x } 100 \qquad (2)$$

Calculation of benzo[a]pyrene equivalency (BaPeq) concentration: The BaP equivalency concentration is a calculation that sums together carcinogenic PAHs compound based on the individual PAHs compound toxic equivalency factors (TEFs), using BaP as a reference value of 1. The individual PAHs TEFs value was adapted from Nisbet and Lagoy as these TEFs have been demonstrated to be a better reflection of the actual state of knowledge on the toxic potency of each individual PAH species relative to BaP[9]. The BaPeq concentration is calculated by summing together each species concentration multiplies by its respective TEFs[10].

Results and Discussion

Concentration profile of PAHs: The fluorescence responsive PAHs found in PM10 are (Ace), (Flu), (Phen), (Pyr), (Chr), (Anth), (BaP) and (Flt)**.**The concentration of total PAHs ranged between 2.67-17 ng m^{-3} during winter, summer and post-monsoon season respectively. The concentration of total PAHs in winter showed highest concentration (17 ng m^{-3}). During summer, the PAHs concentration ranged between 2.51-3.79 ng $m^{-3}$with an average of 2.96 ng m^{-3}. In post-monsoon season, the concentration of total PAHs ranged between 1.63-3.59 ng m^{-3} with an average of 2.74 ng m^{-3}. In all the seasons, the low molecular weight PAHs compounds concentration was observed to be low which may be due to higher tendency to evaporate. These PAHs compounds have a high vapor pressure and also have tendency to exist in the gas phase, thus easily evaporated as compared to higher PAHs. The low molecular weight PAHs which were lighter tend to remain in the gaseous phase than the particulate phase aerosols[11].

Diagnostic Ratio of PAHs: PAHs have been used as tracers to distinguish between multiple sources[12]. Different PAHs concentration and their seasonal variation pattern of individual PAHs vary with different pollution sources, for example, Phen, Fluo and Pyr are characteristics of coal combustion; BaP and Fluo are tracers for wood combustion and fluo, Pyr for heavy duty diesel vehicles[13]. Diagnostic ratios of PAHs generally show the characteristics of the specific source, but care must be taken since they could vary in different ambient atmosphere due to the reactivity of some PAHs species, such as the photo-decomposition of BaP etc. Characteristics diagnostic ratio of PAHs from rural environment are given in table-1. In this study, the ratio of Pyr/BaP was observed as 0.43, 0.39 and 0.37 during winter, summer and post-monsoon season reason respectively which may be due to the variation of BaP concentration in the air because of its photo decomposition. Ratios of Flu/(Flu+Pyr) observed as 5.9,1.16 and 1.38 during winter, summer and post-monsoon season. All the values are greater than 0.5 insighting contribution from coal and wood combustion sources used for domestic purposes whereas ratio less than 0.5 indicates automobile sources. Ratio of Anth/(Anth+Phen) has been used to identify the importance of petrogenic sources. The present study show ratio of 0.43, 0.51 and 0.59 during winter, summer and post-monsoon season respectively. The values observed were >0.10 are typically associated with fossil fuel used for cooking purposes which is a tradition in rural environment. Most of the diagnostic ratio suggested that significant contribution of coal and wood combustion sources. It may be mentioned that a major fraction of PAHs concentration in the atmosphere of rural environment originated from coal and biomass burning in winter and summer and summer seasons however in winter especially, coal, wood and biomass burning is one of the major source of PAHs emissions in rural environment since it is the sources of thermal protection for poor people in the chilling winter[14].

Potential Toxic Fraction of Total PAHs: BaP and Chr are the notified probable carcinogenic PAHs as per USEPA, while the other PAHs studies are not classified as carcinogens. The sampling station showed 15.5, 53.8 and 50.9 % of toxic fraction in winter, summer and post-monsoon season respectively (table-2). The higher toxic fraction was observed during summer followed by post-monsoon and winter season. Based on observation, it was found that 53.8% of total PAHs fraction in aerosols are probable carcinogenic and hence, it could be concluded that most of the probable human carcinogen are found to be associated with aerosols in rural environment. This may be attributed to percentages of higher molecular weight PAHs compounds which were relatively higher in the summer as compared to other seasons. The reported studies in Flanders showed 55% toxic fraction[15].

Benzo(a)pyrene equivalent (BaPeq) concentration: Toxic equivalency factor (TEFs) of the individual PAHs have been used to estimate carcinogenic potential of benzo(a)pyrene equivalence. The TEFs values obtained for selected PAHs during winter, summer and post-monsoon season are given intable-3. The concentration of BaPeq for the seasons were averaged to estimate the annual concentration of Bapeq and was 0.40 ng m^{-3}. The BaPeq concentration were low as compared with other reported studies, viz. Sierra leone West Africa (12.90ng m^{-3}), Tarrogona Spain Agra (88.50 ng m^{-3}), Liaoning (40.05 ng m^{-3}), Florence (0.916 ng m^{-3}), Zonguldak (14.1 ng m^{-3}) and Nanjing (7.1 ng m^{-3}) [16-22]. The estimated BaPeq concentration in the study area is at low pollution risk especially to human health.

Conclusion

Eight PAHs were identified and quantified in the PM_{10} during winter, summer and post-monsoon season. It was observed that PAHs were higher in winter as compared to other season. The dominance of 4 membered ring PAHs in samples indicates that coal, wood and biomass combustion sources were predominant in rural environment. The diagnostic ratios of PAHs calculated in this study further helps in use of PAHs ratio as an indicator of PAHs sources and origins. All aerosol samples shows the presence of BaP which is a signature of PAHs compounds associated with incomplete combustion of coal, wood and biomass. Estimation of health risk associated with exposure to these compounds was made by using BaPeq than using the simple concentration of BaP. The potential BaPeq based on total concentration is 0.40 ng m^{-3} which is lower than limits of 1 ng m^{-3} for BaP standard by regulatory agency.

Table-1
Characteristics Diagnostic Ratios of PAHs attributed to Specific Sources

Diagnostic ratios	Winter	Summer	Post-monsoon	Values	Possible sources
Pyr/BaP	0.43	0.39	0.37	0.1	Gasoline
Flu/(Flu+Pyr)	5.9	1.16	1.38	<0.5 >0.5	Gasoline, Coal/wood
Anth/(Anth+Phen)	0.43	0.51	0.59	≈0.1	Coal/ Gasoline

Table-2
Potential Toxic Fraction of Total PAHs Concentration

Sampling Locations	Season	Avg. PAHs Conc.	Avg. Chy Conc.	Avg. BaP Conc.	Total Conc.	Toxic Fraction (%)
		(ng m^{-3})				
Akkalkuwa	Winter	17.01	2.02	0.61	2.63	15.5
	Summer	3.2	1.42	0.3	1.72	53.8
	Post-monsoon	2.67	1.17	0.19	1.36	50.9

Table-3
Benzo(a)pyrene equivalent (BaPeq) values using Toxicity equivalent factors (TEFs)

PAHs	TEF	Winter	Summer	Post-monsoon
Acenapthene (Ace)	0.001	0.00174	0.00007	0.00006
Fluorene (Flu)	0.001	0.00225	0.00015	0.00024
Phenanthrene (Phen)	0.001	0.00236	0.00028	0.00024
Pyrene (Pyr)	0.001	0.00357	0.00035	0.00025
Chrysene (Chr)	0.01	0.0201	0.0142	0.0117
Anthracene (Anth)	0.01	0.0087	0.0031	0.0036
Benzo(a) pyrene (BaP	1.0	0.61	0.33	0.19
Fluarenthene (Flt)	0.001	0.00263	0.00022	0.00015
∑BaPeq		0.65	0.35	0.21
Akkalkuwa Avg. BaPeq (ng m^{-3})	0.40			

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