Characterization and Quantification of Polycyclic Aromatic Hydrocarbons in Atmospheric Particulate Matter (PM10 &PM2.5)

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Abstract— Air pollution has significant effect on exacerbation of asthma, allergy and other respiratory diseases. Particulate matter less than 10µm in size can pass through natural protective mechanism of human respiratory system and plays an important role in genesis and augmentation of allergic disorders. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous by products of incomplete combustion or pyrolysis of carbonaceous and organic matter (e.g., tobacco, coal, charcoal, diesel, gas, and wood). PAHs are hydrocarbons with two or more fused aromatic rings and there are several hundreds of these compounds. Airborne particles of organic origin contribute significantly to the total particle burden in the atmosphere, either directly or indirectly by burning of biomass and soil re-suspension. In present study PM10 samples were collected using high volume APM 460 NL sampler. Whereas, APM 550 MFC sampler was used for PM2.5 sample collection. All the samples were collected for 24 hr sampling time at Mumbai city . Analysis of 16 USEPA priority PAHs was carried out using high performance liquid chromatography (HPLC) coupled with photo diode array (PDA) detector. PM10 and PM2.5 with associated PAHs concentrations were compared for annually average. The PM10 and PM2.5 concentrations for 24 hr sampling time were found to be within limit stipulated by National Ambient Air Quality Standards (NAAQS) for most of the samples.

Key words: Atmospheric aerosols, PAHs, HPLC-PDA

I. INTRODUCTION

An aerosol is defined as a colloidal system of solid or liquid particles in a gas. An aerosol includes both the particles and the suspending gas, which is usually air. (Barrie.L.A, (1989). Particulate matter in air with aerodynamic diameters less than 10 micrometers is PM10. PM10 has replaced the total suspended particulate (TSP) standards because many of the larger particles included in the TSP measurement (up to 45 micron) do not penetrate into the lungs and have very little effect on health. Consequently, the PM10 measurement is believed to be a better indicator of actual health risks. Fine particles are those that are less than 2.5 micrometers in diameter (PM2.5). Fine particles can accumulate in the respiratory system and are associated with numerous adverse health effects including decreased lung function and increased respiratory symptoms and disease.

Persistent organic pollutants are group of chemicals which are resistant to photolytic, chemical, and biological degradation, are therefore extremely stable and long lived. Persistent organic pollutants are not only persistent in environment but are also highly toxic and build up (bio-accumulate) in the tissues of animals and humans (Stockholm Convention on persistent organic pollutant(POPs)

In India due to increasing industrialisation and urbanisation increases air pollution in great extent. Concentrations of particulate matter in the ambient air are typically composed of complex mixtures of chemical species, originating from a wide range of natural sources and human activities Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds composed of two or more fused aromatic rings of carbon and hydrogen atoms. These pollutants are generally formed by incomplete combustion of organic materials, as well as through natural and other anthropogenic activities Stern et al (1986). In the atmosphere, they may adsorb and condense on the surface of aerosols (particulate phase) or exist in gaseous phase. PAHs are included in European Community (EC) and in the Environmental Protection Agency (EPA) list due to their mutagenic and carcinogenic properties.(NRC. (1983) This justifies the need to assess the air quality regarding hazardous pollutants in populated and industrialised cities. The increasing atmospheric burden of urban particulate matter intermingles with the natural and anthropogenic emissions in the rural areas and the total mixture is eventually transported to the global atmosphere. Concentration of particulate matter in the ambient air are typically composed of complex mixture of chemical species originating from natural and anthropogenic sourses.among that polycyclic aromatic hydrocarbon are the class aromatic compound found in ambient particulate matter shown by (Larsen and Larsen,1998).

PAHS are ubiquitous pollutant in urban atmosphere (Tekasarkul et al.,1991) Also great deal of research has been conducted to investigate the concentration of organic compound in ambient air particulate matter using variety of approaches.

In the current study we have collected air particulate sample on fibre filter paper using high volume sampler, then analysed them for PAHS. Present study assess distributions of chemical components and associated characteristics in air particulate matter.

II. Objectives

1) Sampling of atmospheric aerosols in Mumbai city.
2) To standardize the methodology for estimation of organic pollutants in respirable suspended particulate matter using chromatographic techniques.
3) To Characterize and quantify emerging organic pollutants i.e polycyclic aromatic hydrocarbons (PAHs)
4) To assess distributions of chemical components and associated characteristics in air particulate matter. This would be helpful to identify areas of enhanced concentrations of contaminants, and allow interpretation in terms of relative degrees of contamination and location of sources.
5) To assess annual temporal changes in the chemical composition and physical properties of air particulate at

a specific location through repeated sampling. This would provide the yearly trend of changes in air quality over the city of Mumbai city .

6) To investigate source characteristics and attempt to establish the correlation between various patterns of these pollutants concentrations to that of their probable sources.

III. MATERIAL AND METHODOLOGY

A. Sampling Site and Sample Collection

In the present study PM10 samples are being collected on quartz fibre filter papers using high volume sampler at Mumbai city . which is a representative of typical industrial site with few residences and is near highway. The site may have direct impact of industrial emissions, vehicular traffic and household burning activities.

B. Extraction and Analysis of PAHs

The filter papers were extracted thrice with HPLC grade n-hexane (Merck) by ultrasonication for 1h to ensure complete recovery. The temperature of the water bath was during the ultrasonic-cation kept below 40 °C to avoid any possibility of breakdown of the analyte species. The samples were filtered, pooled and the extracts were concentrated to about 1 ml and then subjected to undergo clean-up process.

C. Analysis

The characterization and quantification of analytes will be done by a high performance liquid chromatography system. and also by gas chromatography. The HPLC analytical column is of 250 mm length and 4.6 mm id., packed with totally porous spherical RP-18 material (particle size 5 µm). A guard column which is packed with RP-18 material (10 mm long and 4.6-mm id.) precedes the analytical column. While gas chromatographic analysis will involve DB-5 cappillary column in programming mode.

D. Quality Control

After 24 h sampling, all the filter papers are stored at 4°C and are analysed within 15 days from collection. Field blank filters are collected to reduce the gravimetric error during sampling and filter paper handling. Quantification of PAHs is carried out by comparing the retention times and peak areas of the samples with standards. Several dilutions corresponding to 0.2 to 20 ng absolute of synthetic standard mixture of individual component of PAHs, supplied by Supelco, USA, dissolved in HPLC grade acetonitrile is used for determining the retention data and for studying the linearity of the detector. For quality control, method blanks (solvent) and spiked blank (standards spiked into solvent) will be analysed in the same manner that samples are analysed.

IV. INSTRUMENTATION OF HPLC SYSTEM

Measurements were carried out using a HPLC system shimadzu (LC-10 AD) with UV-visible detector. The analytical column was of 250mm length and 4.6mm internal diameter, packed with totally porous spherical Reverse Phase C-18 material (particle size 1um) with a guard column (10mm long and 4.6mm i.d) preceded the analytical column. Acetonitrile-water mixture (75:25) was used as mobile phase at a flow rate of 1.0ml per minute. Samples 0.1ul were injected into the column through the sampling loop. A UV detector set at 254nm for absorption was used for the detection of the compounds. The data was processed using a PC based Chromatography Interface Software (JascoBorwin, Japan).

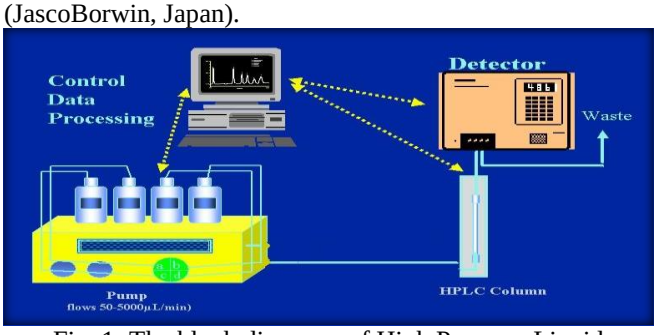

Fig. 1: The block diagrams of High Pressure Liquid Chromatography (HPLC)

Instrument	HPLC model LC-10 AD, Shimadzu Japan
Analytical column	C-18 column (5µm totally porous Octadecylsilane packing, Merck Germany), 250mm×4.6mm i.d. with a C-18 guard column.
Mode	Reverse phase, Isocratic
Detector	JASCO PDA MD2015plus 200-800nm(254nm for quantities analysis)
Mobile Phase	Acetonitrile: water (85:15)
Flow rate	0.80ml/min

Table 1: HPLC parameter for PAHs analysis.

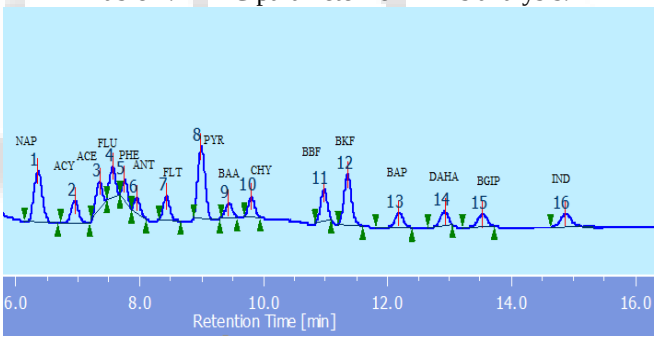

Fig. 2: The chromatogram of the PAHs standard samples analyzed in High performance liquid chromatography

V. RESULT AND DISCUSSION

Result of the experimental work carried out is presented .The details included varying concentration of different PAH compounds. Twenty -four hour sampling period was chosen a sample for PM_{10} were collected during the study period. Characterization and quantification of annually average and variation in mass concentration of total PAHS in PM 10 and PM 2.5 whereas the estimation of PAHs was done by chromatograph.

A. PM $_{10}$ and $PM_{2.5}$

1) Annual Average Dust Load In PM_{10}:

The annual air particulate dust load in Respirable suspended particulate matter (PM_{10}) is shown in figure 5.1. Maximum annual concentration of Respirable suspended particulate matter for the studied year varied from 33.6 to 108.52µg/m^3. During the study period, maximum PM_{10} dust load was observed in the month of January with average value of 108.52 µg/m^3.Seasonwise, maximum concentration was

observed in winter (October-January). During this study average annual average value in Respirable particulate matter (PM_{10}) was 66.31 µg/m^3. Average annual limit of CPCB for Respirable particulate matter (PM_{10}) is 60 µg/m^3. At present study location the annual average of Respirable suspended particulate matter (PM 10) was more than CPCB limit

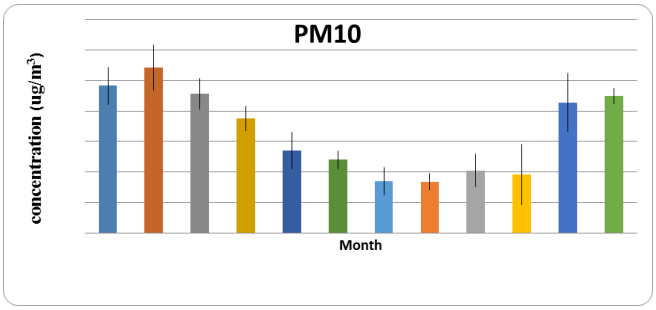

Fig. 3: dust load in Respirable particulate matter (PM_{10})

2) Annual Average Dust Load In PM2.5:

Mass concentrations of fine particulate matter having aerodynamic diameter equal to or less than 2.5µm ($PM_{2.5}$) during the sampling period are shown in Fig 5.2. Fine particulate matters mass concentration was found to vary from 22 to 62.32 µg/m^3. A minimum PM2.5 concentrations was observed in June with average of 22µg/m^3, while maximum concentration of fine particulate matter was observed in December with average value of 62.32 µg/m^3.

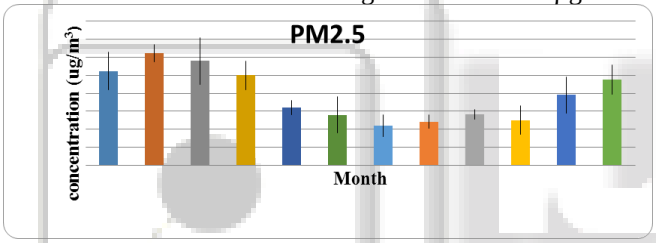

Fig. 4: dust load in fine particulate matter ($PM_{2.5}$)

B. Ratio of PM $_{2.5}$and PM$_{10}$:

PM 10 is the size of air particulates that are inhaled by us during respiration, while PM2.5 is the fine fraction of this Respirable mass which reaches to up to the alveolar region and thus possess a greater health threat. $PM_{2.5}/PM_{10}$ ratio is important parameter for determining sources of air particulate matter and to know the coarse and fine fraction contribution in total mass of PM. Annual PM2.5/ PM10 ratios are depicted in Fig. 5.3. $PM_{2.5}$ to PM_{10} ratio varied from 0.45 to 0.72 which indicates contribution of fine particulate matter to about 45-72% of the Respirable dust (PM_{10})

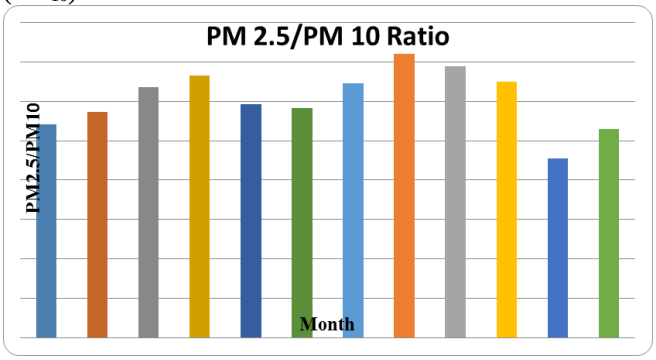

Fig. 5: $PM_{2.5}/PM_{10}$Ratio in air particulate matter

1) Total PAHs in PM$_{10}$:

Polycyclic aromatic hydrocarbons associated with PM_{10} were estimated using HPLC-PDA after ultrasonic extraction of APM laden filter papers. Sixteen PAHs including EPA priority were monitored in air particulate matter viz. Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLT), Pyrene (PYR), Benz[a]Anthracene (BAA), Chrysene (CHY), Benzo[b]fluoranthene (BBF), Benzo[k]fluoranthene (BKF), Benzo[a]pyrene (BAP), Dibenz[a,h]Anthracene (DAHA), Benzo[ghi]perylene (BGIP), Indeno[1,2,3-cd]pyrene (IND). PAHs were found to be in high concentration in winter and low concentration in monsoon. Concentrations of PAHs follow similar annual trend as that of particulate matter. Figure 5.4 shows that maximum Total PAHs concentration in January and December was 37.34µg/m3and 32.15µg/m3 respectively whereas minimum concentration was observed in July and August with average concentrations of 9.32µg/m3and 9.55µg/m3 respectively. Dust load and PAHs were observed more in winter, may be because of more domestic and other burning activities in winter. Likewise, minimum concentrations were found in monsoon because of less burning and aerosol washout in Monsoon. PAHs are formed at high temperature when organic compounds are partially cracked to smaller unstable molecules. At high temperature during burning of organic compounds easily breaks C_C and C-H Bond to yield free radicals, these radicals combine together to form large molecule and form aromatic ring i.e. PAHS

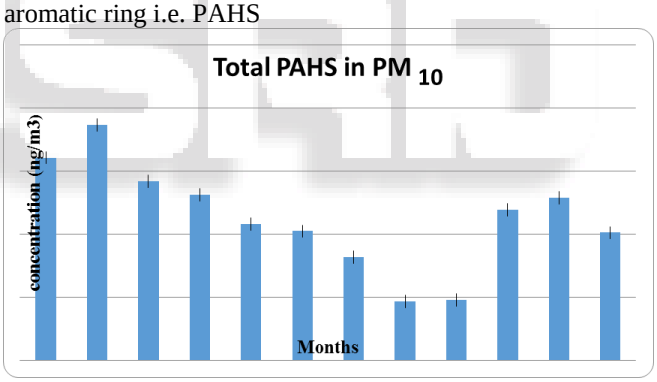

Fig. 6: Total PAHS in PM_{10}

VI. Conclusion

In present study it was clearly observed that the particulate matter especially the Repairable Particulate Matter (PM_{10}) and (PM 2.5) was exceeding the annual limits set by CPCB in India. Particulate matter or aerosolsare considered to be most important because of theirpotential health hazards. The PM_{10} and PM2.5 samples were collected over a period of one year, they were chemically processed and analyzed using chromatographic techniques.

Assessment of the fraction of air particulate matter especially the RSPM which we breath is very important for evaluation of various health hazards associated with it and for making policies for mitigation of the sources if the levels are more. The assessment involves both physical and chemical characterization using various analytical techniques that starts from recognition of the problem to planning through sampling, processing, analysis and data interpretation.

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