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CONCENTRATIONS AND CARCINOGENIC POTENCIES OF ORGANIC POLLUTANTS (PAHS) IN PM_{10} AT A SEMI ARID REGION OF INDIA

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ABSTRACT

Atmospheric aerosols are ubiquitous in the troposphere and play an important role in climate and atmospheric chemistry. They include inorganic and organic chemical species, which could have harmful effects on human health. Aerosols resulting from the emission of harmful gases and particles are serious environmental air pollution problems in many of the world's urban areas. Atmospheric particulate matter from four different areas within Agra city(a semi-arid region) were collected using respirable dust samplers during the 2006 summer season and were then extracted with dichloromethane using an automated Soxhlet Extraction System (Soxtherm®). The extracts were analyzed for 17 target Polycyclic Aromatic Hydrocarbons (PAHs). The total PAH (TPAH) concentrations were 76.6 ± 3.6, 27.9 ± 2.9, 23.7 ± 2.3 and 6.5 ± 1.7 nanograms per cubic meter (ng m^{-3}), respectively, at the industrial, residential, roadside and agricultural sites. The combined mean concentration of TPAH was 33.9 ng m^{-3} for all sites. The industrial site had the highest TPAH concentration followed in order by the residential, roadside and agricultural sites. Indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene and benzo(b)fluoranthene were the predominant compounds found in the samples collected from all of the sites. The carcinogenic potencies related to PAHs have been calculated by using Toxic Equivalent Factors (TEFs) compiled from the literature which corresponds to a B (a)P equivalent exposure of 8.9 ng m^{-3} and 8.6 ng m^{-3} with respect to carcinogenicity.

Keywords: *PAHs, Semi Arid Region, Particulate Pollution, Toxic Equivalent Factor*

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are chemicals containing two or more fused benzene rings in a linear, angular or cluster arrangement. PAH contain only carbon and hydrogen. They belong to the group - Persistent Organic Pollutants (POPs) known for their chemical carcinogenicity. They are formed during incomplete combustion of organic materials and geochemical formation of fossil fuels and are the products of thermal decomposition. Sources of PAHs include automobiles, re-suspended soils, refineries and power plants. It is well established that some PAHs have carcinogenic, mutagenic and immunotoxic effects on animals and can occur in low concentration in many parts of the environment (Grimmer, 1983). Due to their mutagenic and carcinogenic potential the atmospheric concentrations of PAHs in many geographical locations of the world have been measured and reported, e.g. Massachusetts, USA (Allen et al, 1996) Ontario, Canada (Katz et al, 1978), Athens, Greece (Viras et al, 1987), Antarctica (Caricchia et al, 1999), Lahore, Pakistan (Smith et al, 1996) and even in Mumbai, India (Kulkarni and Venkataraman,2000). In many circumstances the environmental occurrence of PAHs has been associated with adverse effects on public health (Grimmer, et al, 1983). Atmospheric PAHs are partitioned between the particulate matter and gas phases, depending on the PAH molecular weight. Low molecular weight PAHs have higher concentrations in the vapor phase while high molecular weight PAHs are often associated with particles. It is believed that there is no "*Threshold*" or "*Safe*" level for the mutagenic compounds, hence exposure to these PAHs at any level provide the risk of toxic effects.

Nowadays, there is a lot of concern about air quality in large urban areas, and it has been the subject of many studies. The harmful effects of Polycyclic Aromatic Hydrocarbons (PAHs) on human health have been especially studied, since some of these are carcinogenic and mutagenic, and some are associated with acute and chronic health problems (Dallarosa et al., 2005, Fang et al., 2004). PAHs are organic compounds of carbon and hydrogen arranged in combinations of aromatic rings. The contribution from natural sources of PAHs is limited, being restricted to spontaneous forest fires and volcanic emissions (Bourotte et al, 2005). In cities, the sources of PAHs are exclusively anthropogenic, i.e. they are formed during incomplete combustion and pyrolysis of organic matter, such as coal, oil, wood and fuels like diesel and petrol. Automobile exhaust has been recognized as the major PAHs contributor in urban areas (Velasco et al., 2004). Their elevated concentrations in urban environments pose a risk of exposure to inhabitants (Sienra et al., 2005).

In Agra the most important source of PAHs is expected to be vehicular emission since motor vehicles contributed as much as 60% of pollution. As of August 2006 there were 3, 36,635 registered vehicles in Agra (News item, Amar Ujala, 2006). There are also other important potential sources of PAHs such as smoke coming from diesel generators which are 32,030 in Agra and are in use because of erratic power supply. The concentration determined for individual PAH will help Planners, Scientists, and Administrators to draw strategies to reduce PAH exposure to the people living in this area. The aim of this study is to investigate the concentration and distribution of particulate PAHs in Agra.

METHODOLOGY

Air sampling stations were set up in the four locations, representing industrial, residential, roadside and agricultural areas, were selected for study. Each station was monitored for ambient air quality twice a month in a scheduled manner. Particulate Matter (PM_{10}) in air were collected on 20.3 x 25.4 cm^2 glass fiber filter paper (EPM-2000) using respirable dust samplers (RSPM Envirotech Sampler RDS, 460 DX, New Delhi, India) at the rate of 1.0 cubic meter per minute (m^3/min). The air suction rate was verified every week using calibrated rotameters with an accuracy of ±1%. Samples were stored in a cool, dark place until analysis. Samples and blanks were extracted with 140 milliliters (mL) methylene chloride by Soxtherm®. Blank spike/blank spike duplicate (BS/BSD) samples (spiked with PAH spiking solution) were extracted using clean fibreglass thimbles. No surrogates were added. After the samples were extracted for one programmed cycle, 100 mL of additional solvent was added. All samples were extracted for another programmed cycle and then concentrated to 1.0 mL. Internal standards were added to all extracts prior to sample injection. The gas chromatograph (GC) oven was temperature programmed to separate the method analytes on a fused silica column, which were then detected with a mass spectrometer (MS).

RESULTS AND DISCUSSION

Summer season comprises of four months i.e. from March to June. The atmospheric pollution load is high and because of the down ward wind, pollutants may be transported to the different areas mainly from an oil refinery situated in Mathura (50 kms from the centre of Agra City). This period is often characterized by strong dust storms caused due to low pressure developed in this area. The temperature and relative humidity ranges from 15.4°C to 48.8°C and 18.4%-62.7% respectively. The down ward wind is west and north-north-west and its speed ranges from 0.2 m s^{-1} to 9.2 m s^{-1} in summers (Parivesh, 2006). **Table 1** illustrates the individual concentrations of PAHs at different locations. The TPAH concentrations were 76.63, 27.96, 23.79 and 6.54 ng m^{-3} at industrial, residential, roadside, and agricultural sites, respectively. The combined mean concentration of TPAH was 33.95 ng m^{-3} for all sites. The industrial site had the highest TPAH concentration followed by the residential, roadside and agricultural sites. These results also indicate that PAH concentrations are strongly linked to land use.

The concentration trends of the major PAH found in present study are illustrated in **Figure 1**, which were: benzo (g,h,i)perylene > indeno(123-cd) pyrene > benzo(b)fluoranthene > benzo(a)pyrene at the industrial site; benzo(b)fluoranthene > indeno(123-cd)pyrene > benzo(k) fluoranthene > benzo(g,h,i)perylene at the residential site; benzo(g,h,i)perylene > benzo(b)fluoranthene > benzo(a)pyrene > indeno(123-cd)pyrene at the roadside site: and benzo(g,h,i)perylene > indeno(123-cd)pyrene > benzo(k)fluoranthene > benzo(b)fluoranthene at the agricultural site. At all the sites, indeno (123-cd)pyrene, benzo(g,h,i)perylene, and benzo(b)fluoranthene were the predominant compounds.

Figure 2 shows the relative contribution of 2-, 3-, 4-, 5-, and 6-ring PAHs in the atmosphere at the locations investigated in this study. The average TPAH percentage based on the number of rings were 0.67% (2-ring), 3.41% (3-ring), 21.72% (4-ring), 41.18% (5- ring), and 33.05% (6-ring). The major contributors to TPAH in the Agra region were 5-ring and 6-ring PAHs (41.18% and 33.5% of the TPAH respectively).

An occupational exposure limit for TPAHs has not been established because of the complex chemical composition of PAH mixtures. Several PAH species including benzo(a)pyrene (the most carcinogenic compound) have been classified as probable (2A) or possible (2B) human carcinogens by the International Agency for Research on Cancer (IARC, 1987). B(a)P is a five ring ($C_{20}H_{12}$) compound, is mutagenic for human cells in culture (Osborne et al., 1987) and carcinogenic in whole animal assays (Cerna et al., 2000). One approach to estimating the carcinogenic potency associated with exposure to a given PAH compound is to assign a Toxic Equivalent Factor (TEF), a measure of its potency relative to that of B(a)P. The TEF for B(a)P is set at 1.0 (Bostrom et al., 2002). The concentration of each individual PAH compound is multiplied by its respective TEF to calculate the "B (a)P equivalent", or $B(a)P_{eq}$ concentration. The TEF approach has the main advantage of being relatively easy to apply, but it may underestimate risk because only a limited number of PAH compounds have assigned TEFs (WHO/IPCS, 1998). Two lists of TEFs, compiled by Tsai et al., (2004) and EPA Region III (2006), were used in this study.

Table 2 indicates the mean concentration of TPAHs in Agra to be 33.6 ng m^{-3}, which corresponds to a B(a)P equivalent exposure of 8.9 ng m^{-3} and 8.6 ng m^{-3} with respect to carcinogenicity, using TEFs given by Tsai et al. (2004) and EPA Region III (2006), respectively. Regardless of the TEF source, similar B(a)P exposure estimates were generated by the two sets of TEF values.

CONCLUSION

The TPAH concentrations were 76.6 ± 3.6, 27.9 ± 2.9, 23.7 ± 2.3 and 6.5 ± 1.7 ng m^{-3} at industrial, residential, roadside, and agricultural sites, respectively. The combined mean concentration of TPAH was 33.95 ng m^{-3} for all sites. The industrial site had the highest TPAH concentration followed by the residential, roadside and agricultural sites. These results also indicate that PAH concentrations are strongly linked to land use. The average TPAH percentage based on the number of rings were 0.67% (2-ring), 3.41% (3-ring), 21.72% (4-ring), 41.18% (5- ring), and 33.05% (6-ring). The major contributors to TPAH in the

Agra region were 5-ring and 6-ring PAHs (41.18% and 33.5% of the TPAH respectively). The result shows that the variation in the concentration of PAHs depends on different locations. The mean concentration of TPAHs in Agra to be 33.6 ng m^{-3}, which corresponds to a B(a)P equivalent exposure of 8.9 ng m^{-3} and 8.6 ng m^{-3} with respect to carcinogenicity. It is also clear that much variation is found in industrial and agricultural sites whereas the residential as well as roadside sites have almost similar concentration of PAHs.

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Table 1: Individual concentrations of PAHs at different locations (ng m^{-3})

PAHs	**IND**	**RES**	**RDS**	**AGR**
NAP	0.2	0.12	0.22	0.07
ACY	0.71	0.13	0.2	0.08
ACE	0	0	0.19	0
FLU	0.21	0.11	0	0
PHE	1.53	0.24	0.33	0.1
ANT	0.31	0.18	0.16	0.08
FLT	2.09	0.94	1.14	0.43
PYR	3.26	1.35	1.06	0.51
B(a)A	2.71	1.14	1.82	0.47
CRY	2.07	2.16	1.62	0.55
B(b)F	9.43	4.35	3.03	0.63
B(k)F	5.74	3.62	2.41	0.67
B(e)P	6.65	2.72	1.65	0.56
B(a)P	8.52	2.76	2.94	0.42
IND	11.63	3.8	2.72	0.69
DIB	2.11	1.13	1.12	0.18
B(ghi)P	19.46	3.21	3.18	1.1
TOTAL	**76.63**	**27.96**	**23.79**	**6.54**

Table 2: BaP toxic equivalency factors (TEFs) and BaP_{eq} exposure profiles (ng m^{-3})

PAHs	MEAN	*TEFs	BaP exposure	$^{+}$TEFs	BaP exposure
Naphthalene	0.1525	0.001	0.0001525	--	--
Acenaphthylene	0.28	0.001	0.00028	--	--
Fluorene	0.08	0.001	0.00008	--	--
Phenanthrene	0.55	0.001	0.00055	--	--
Anthracene	0.1825	0.01	0.001825	--	--
Fluoranthene	1.15	0.001	0.00115	--	--
Pyrene	1.545	0.001	0.001545	--	--
Benzo(a)anthracene	1.535	0.1	0. 1535	0.1	0. 1535
Chrysene	1.6	0.01	0.016	0.001	0.0016
Benzo(b)fluoranthene	4.36	0.1	0.436	0.1	0.436
Benzo(k)fluoranthene	3.11	0.1	0.311	0.01	0.0311
Benzo(e)pyrene	2.895	1	2.895	1	2.895
Benzo(a)pyrene	3.66	1	3.66	1	3.66
Indeno(1,2,3-cd)pyrene	4.71	0.1	0.471	0.1	0.471
Dibenz(a,h)anthracene	1.135	1	1.135	1	1.135
Benzo(g,h,i)perylene	6.7375	0.01	0.067375	--	--
TOTAL	**33.6**		**8.9**		**8.6**

**TEFs cited by Tsai et al. (2004), $^{+}$TEFs cited by EPA Region III (2006)*

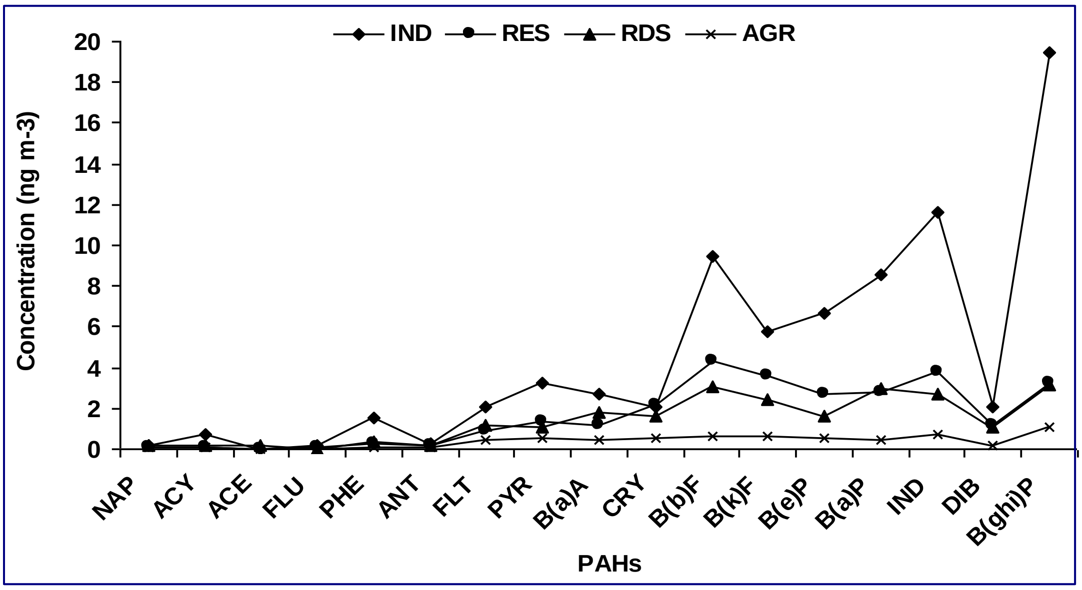

Figure 1: Trends of individual concentrations of PAHs in ambient air at different sites of Agra (ng m^{-3}) during summers

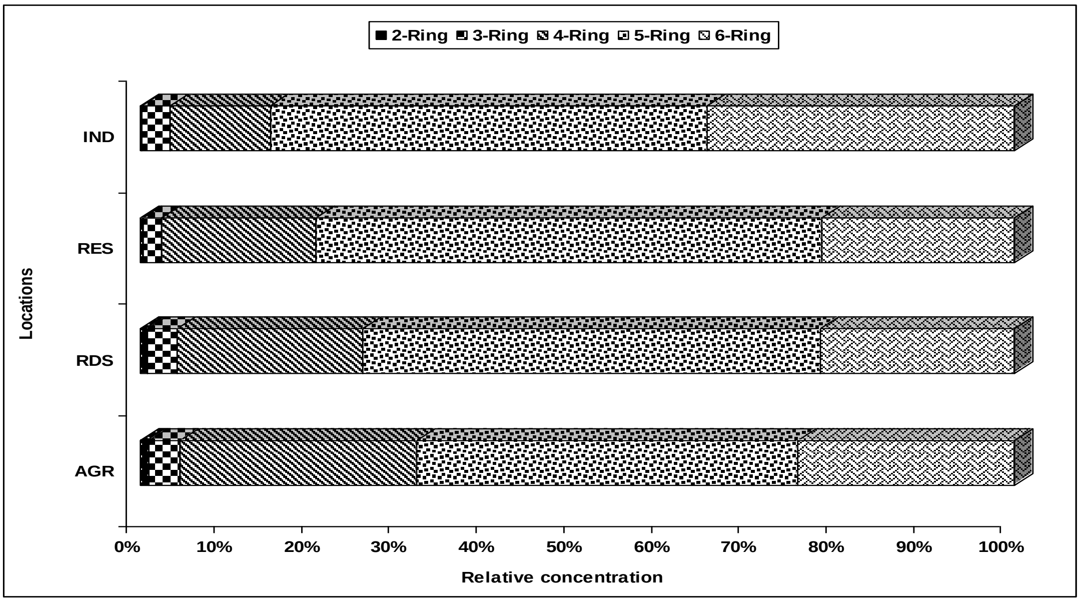

Figure 2: Distribution of PAHs based on benzene ring at different locations of Agra in summers