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STUDIES ON PRESENCE OF PAHs IN AMBIENT AIR OF NAGPUR CITY (INDIA)

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ABSTARCT

Polyaromatic hydrocarbons often are by product of petroleum processing or combustion. Many of these compounds are highly carcinogenic at relatively low levels. Highly carcinogenic & mutagenic compounds such as Poly Aromatic Hydrocarbon (PAH's), Poly Chlorinated Biphenyls (PCB's), Alkenes, Olefins etc. are emitted into the atmosphere as a result of incomplete combustion of fuel. Among the various organic pollutants in air, PAHs are the largest single class of known carcinogens. They are a class of organic fraction associated with suspended particulate matter (SPM) and are widely disseminated throughout the atmosphere. Both forms, in gaseous state as well as in particulate matter in bounded form can be inhaled into the lungs. Out of sixteen PAH's Benzo(a) Anthracene [B{a}A], Benzo (b) Flouranthene [B{b}F] and Benzo (a) Pyrene [B{a}P] are known to be potentially weak, and moderate carcinogenic selected for this study. This report presents the profile of PAH, monitored in the particle bound ambient air of Nagpur City in Maharashtra. Respirable dust and Fine Particulate Sampler collected the ambient air particulate on the filter paper. Extracted samples were analyzed by capillary Gas Chromatography using FID. During study period it was observed that B(a)A concentration ranging from 0.0 to 1.56 ng/m^3, B(b)F concentration ranging 0.0 to 1.28 ng/m^3 and B(a)P was ranged from 0.0 to 1,01 ng/m^3. During the winter season the concentration of PAH's recorded higher as compare to monsoon & summer seasons. This might be due to foggy conditions in winter.

Keywords: Ambient air, pollution, PAHs, Health, Management

INTRODUCTION

One of the adverse effects of the profuse use of fossil fuels by man now-a- days is ubiquitous presence of Polycyclic aromatic hydrocarbons (PAHs) in the environment in relatively high concentrations. There is no indication that the input of these compounds into the environment as a result of human activities will decrease sustainably inn the next decades. Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of compounds and hundreds of individual substances may be released during incomplete combustion or pyrolysis of organic matter which is an important source of human exposure. Studies on various environmentally relevant matrices, such as coal, combusted effluent, motor vehicle expects, used motor fabricating oil and tobacco smoke have shown that the presence of PAHs in these mixtures is mainly responsible for the carcinogenic potential .Numerous paper and review have been published on the occurrence, distribution and transformation of PAHs in the environment and its ecotoxicological and toxicological effects[1].

In general, any organic compound containing two or more aromatic rings may be considered to be a more aromatic matter. The term “Poly cyclic aromatic hydrocarbon” commonly refers to a large class of organic compound containing two or more fused aromatic rings made up of carbon and hydrogen atoms. At ambient temperature, PAHs is solids. The general characteristics common to the class of high melting and boiling points, low vapor pressure and very low water solubility which tends to decrease with increase molecular mass. PAHs are soluble in many organic solvents and are highly lipophilic. They are chemically rather inert.

Temperature has a significant influence on the solubilities of PAHs. In the presence of light and oxygen PAHs readily undergo photo-oxidation. Reactions that are of interest with respect to their environmental fate and possible sources of loss during atmospheric sampling are photodecomposition and reaction with nitrogen oxides, nitric acid, sulfur oxides, sulphuric acid, ozone and hydroxyl radicals.
The PAHs principally are used as intermediate in the production of PVC's and plasticizers (nathalene) Pigments (acenapthelene, pyrene), dyes (anthracene, flouranthene), and pesticides (Phenentherene). The largest emissions of organic materials during industrial processes and other human activities including-

1. Processing of coal, crude oil and natural gas, petroleum refining and production of carbon blacks, creosol and coal tar.
2. Aluminum, iron and steel production in plants and foundries.
3. Heating in power plants and residence and cooking.
4. Combustion of refuse
5. Motor vehicle and
6. Environmental tobacco smoke

Several distribution and transformation process determine the fate of both individual PAH and mixture.Partitioning between water and air, between water sediment and between water and biota are the most important distribution process. . PAHs are photo oxidized in air and water in the presence of sensitizing radicals like OH, NO_3 and O_3. PAHs are ubiquitous in the environmental and various individual PAHs have been detected in different compartment in numerous studies. In air the levels of individual PAHs tend to be higher in winter than in summer by at least one order of magnitude. The predominant source during winter is residential heating while during summer is urban motor vehicle traffic. Several studies have been carried out on the PAHs in general and B (a) P in particular for their carcinogenic effects, solubility in tissue fluids and plasma proteins[2]. Combustion of fossil fuels is the dominant source of PAHs occurring in the environment. PAHs are highly lipid soluble showing less tendency towards bioaccumulation in the fatty tissue; the lungs and gut of mammals to metabolize rapidly absorb them. The increase in pollution level of these compounds will increase the possibility of cancer patients[3]. In biota uptake process for PAHs are related to their hydrophilic character. Due to above environmental significance, ambient PAHs concentration scenario has been elaborated and include entire Nagpur region for PAHs study from April 2010 to March 2011which is one of the most growing city of Central India.

EXPERIMENTAL

Study Area

Nagpur has been an important city of India, since the 18th century, but it came into prominence only after 1956 being the second capital city of Maharashtra and due to its geographical location and progress in industrial, educational and cultural sectors. The development in various avenues like two major rail link junctions, chamber of commerce, Rastra Sant Tukdoji Maharaj Nagpur University, Nagpur Improvement Trust, Winter assembly session of the Government of Maharashtra, Textile mills, Air force Command, Ambajari Ordnance Factory, Central Reserve Police Force camp, Maharashtra Industrial Development Corporation and MIHAN are just a few of Nagpur achievements.
The total area of the city was only 217.56 Sq. Km. at the time of the establishment of Nagpur Municipal Corporation in 1951. At that time only 42 wards were demarked. However, in 1968, the city was redivided into 75 wards due to rapid growth in its population. According to Census 2011, population of the Nagpur district was 23, 98,165 (Table 1 and Fig.1). In addition to this, the city has grown in length and breadth and today the total vehicle population in the city has grown to more than 10 lakhs indicating the progress and improvement in the living standard along with the problems of environmental concerned.
In the present study, samples were collected from different areas of Nagpur City, India. These areas included, Sakkaradara Square (busy traffic area with high commercial activity), which was selected for monitoring the levels of particulate matter (PM10). Civil lines and Ramdeobaba Kamla Nehru Engineering College (RKNEC), campus areas were selected as representatives of residential zone as they are surrounded by residential area. MIDC, which is the industrial area, was selected as industrial site

(Plate-1). The particulate matter (PM_{10}) sampler was operated at a height of approximately 5-15mts above the ground level. The details of monitoring sites are presented in Table 2. To understand the extent of exposure of PAHs to urban population, routine monitoring of these compounds has been under taken in the city.

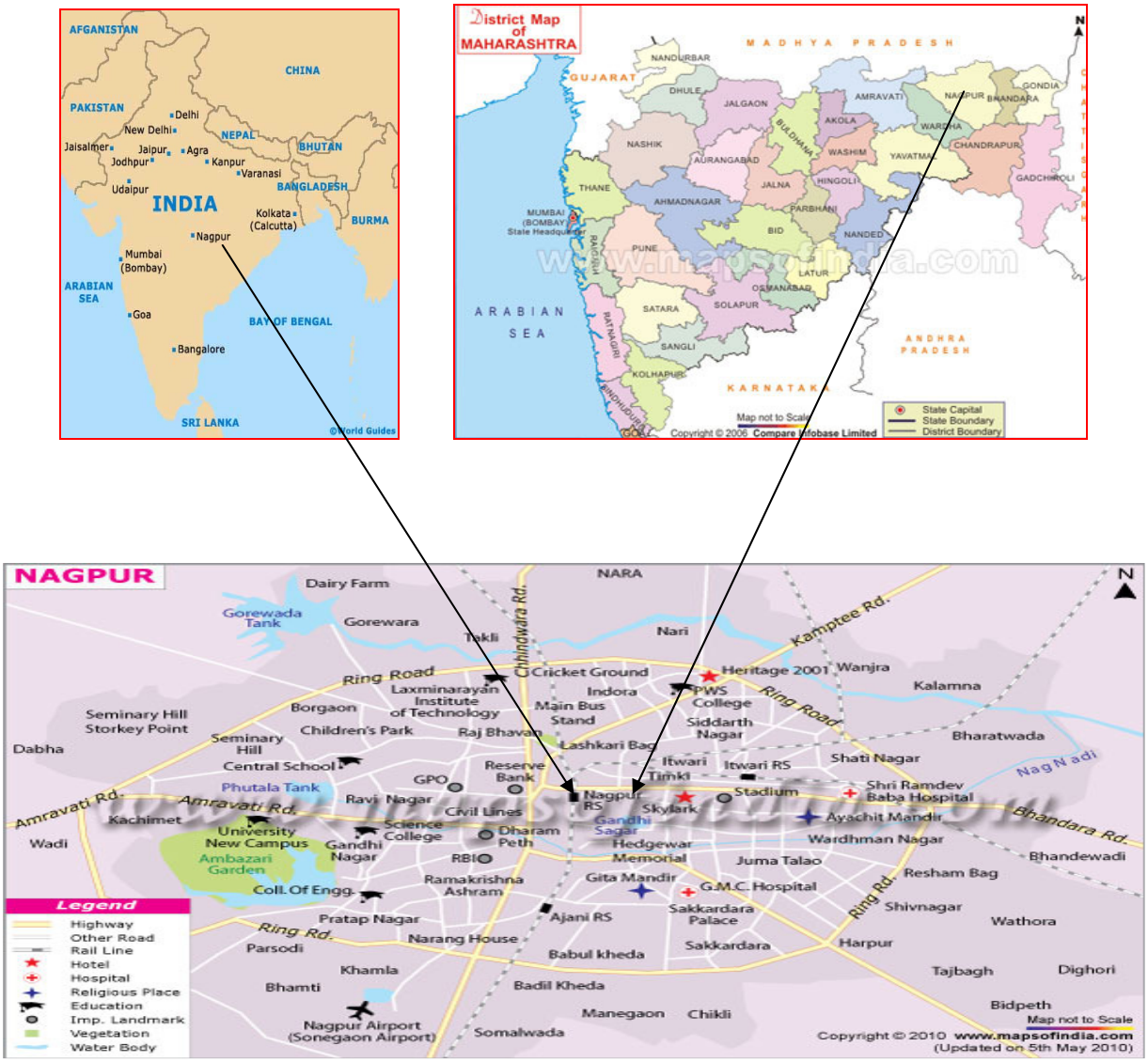


Plate-1: Map Showing Ambient air monitoring stations, Nagpur (Maharashtra), India

Out of sixteen PAHs compounds B (a)A, B(b) F and B(a) P which are known to be potentially weak, moderate and strong carcinogenic respectively were selected for this study[4].

Table-1: Population of Nagpur City

Year	Population
1961	6,43,659
1971	8,66,076
1981	12,19,461
1991	16,24,752
2001	20,52,066
2011	23,98.165

Plate-2: Respirable Dust Sample at Hingna Site

Plate-3: Gas Chromatograph- Mass Spectrophotometer (Shimadzu Make)

Table-2: Details of sampling stations

Site	Location	Activity	Height above the Ground level (meters)
MIDC, Higna	Wadi Naka	Industrial, Vehicular	5
Sakkardara Square	Near Sevaldal Mahavidhalaya	Commercial, Residential, vehicular	15
Civil Lines	Residential Quarters	Residential, Government offices, green belt	5
Katol Road	Near RKNEC	Highway, Residential	5

Table-3: Minimum-Maximum Ranges of SPM in Nagpur City (2009-2010)

S.No.	Area	Location	Minimum	Maximum
1	Industrial	Wadi Naka	110.5	323.0
2	Commercial	Sakkardara Square	106.6	245.5
3	Residential	Campus of RKNEC Civil Lines	81.0	202.0

• All results in $\mu g/m^3$

Table-4: Seasonal Concentration profile of SPM in Nagpur City (2009-2010)

S.No.	Area	Winter	Summer	Post Monsoon
1	Industrial	142.0 – 345.0	154.0 – 458.0	94.0 – 108.0
2	Commercial	115.0 – 516.0	108.0 – 492.0	87.0 – 218.0
3	Residential	116.0 – 201.0	72.0 – 188.0	92.0 – 198.0

*All results in $\mu g/m^3$

Table-5: Minimum-Maximum Concentration of PAH's in Ambient Air of Nagpur Region (2009-2010)

S. No.	PAHs	Minimum	Maximum	Remarks
1	B (α) A	BDL	1.56	At Sakkardara Square (C/W)
2	B (α) F	BDL	1.28	At Sakkardara Square (C/W)
3	B (α) P	BDL	1.01	At Sakkardara Square (C/W)

All results in ng/m^3
C/W: Commercial/ winter
BDL- Below Detectable Limit

Table-6: Seasonal Concentration profile of PAH's in Nagpur city (2009-2010)

S.No.	PAH's	Winter	Summer	Monsoon
1	B (α) A	0- 1.56	0-1.02	0-0.98
2	B (α) F	0-1.28	0-0.96	0-0.72
3	B (α) P	0-1.01	0- 0.36	0- 0.19

*All results in ng/m^3

Table-7: Different International Standard Limit for Poly Nuclear Aromatic Hydrocarbon[10].

OSHA	Occupational Safety &Health Administration	0.2 mg/m^3	For Ambient Air
NIOSH	National Institute for Occupational Safety & Health	0.1 mg/m^3	For Human Exposure
EU	Europe	5.0 ng/m^3	Benzo (α) Pyrene
GER	Germany	1.3 ng/m^3	Benzo (α) Pyrene
USA	United State of America	03-07 ng/m^3	Benzo (α) Pyrene

Sampling

The samplings of suspended particulate matter were collected on 24 hourly basis in the following shifts:

a. 6.00 am to 2.00 pm
b. 2.00 am to 10.00 pm
c. 10.00am to 6.00 pm

By a Respirable Dust Sampler (RDS) and Fine Particulate Sampler (FPS) at a average rate of 1.5 m^3/min once in week at each location from April 2010 to March 2011.The dust collected was used as the basis material for extraction of organic fraction and its enrichment for the PAHs was performed by using soxhlet extraction, rotary evaporator as discussed in PAHs standard method for air sampling (Plate-2).

Sample Preparation

Suspended and fine particulate matter of diameter >10µm and <10 µm were collected Respirable Dust Sampler (RDS) and Fine Particulate Sampler (FPS) respectively on pre -weighed glass fiber filter paper. The filter papers were in kept in desicator and then weighed. Extraction of PAHs was performed by soxhlet extraction method. Full exposed filter paper was cut in to small pieces with care to avoid loss of dust and put in to 30 ml distillation vessels for 6 hrs using 100 ml cyclohexane in evaporating flask. After extraction; extract was reduced up to 5 ml. If the extract was clear, cleanup was not necessary. Extracted sample was ready for Gas Chromatographic analysis by the method described by Lodge[5].

Capillary Gas Chromatography

Analysis of PAHs compounds has been performed by capillary Gas Chromatograph[6]. For PAHs analysis, sigma 2000 (Shimadzu make) Gas Chromatograph with flame ionization detector (FID) was used. The analysis was carried out under the following experimental conditions-

Column: Recktex, 30 mtrs x 0.25 ID, film thickness 0.50 um (DB-5 ms)
Carrier Flow: Nitrogen 22 psi
Column Temp : 65° C for 1 min. @ 25° C up to 140° C
for 0 min. @ 10° C up to 290 °C for 15 min
Detector Temperature : 300 °C
Injector Temperature : 275 °C

Instrument analysis

Standardization was done using USA Made Poly science standards. Volume of injection was 2 µl and split open after 1 minute of injection .The identification and quantification of sample chromatograms with standards chromatograms were performed by Gas Chromatogram –Mass Spectrometer (GC-MS) {Shimadzu Make) integrator ; chromatograms were also checked manually by overlapping the standards and sample chromatogram (Plate-3)[7].

RESULTS AND DISCUSSION

Trend of analysis of criteria pollutant (Suspended Particulate Matter) of Nagpur city was projected in (Table-3 and Table 4). Air quality status of Suspended Particulate Matter (SPM) in Nagpur city shows that average concentration of SPM is higher in Commercial area followed by Industrial area in 2007-2008. The SPM concentration levels in ambient air are reported minimum value 81.0 µg/m^3 at Residential area and maximum value 323.0 µg/m^3 at Industrial area of Nagpur city. PAHs trend of Nagpur city that all the monitored Polyaromatic Hydrocarbons (PAH's) are present in ambient air during 2007-2008. Out of three PAH compound B(a)A show highest concentration ranging from 0 to 1.56 ng/m^3 followed by B(α)F varying from 0 to 1.28 ng/m^{3}and B(a)P from 0.0 to 1.01 ng/m^3 (Table 5). The seasonal variation of ambient PAHs level shows that the concentration of B(α)A [Benzo Alpha Anthracene] , B(α)F [Benzo Alpha Florescence] and B(α)P[Benzo Alpha Pyrene] was higher in winter as compared to other seasons (Table 6). During summer season, the PAHs compounds are comparatively at low concentration level than winter seasons. This is attributed due to high temperature in summer, which is responsible in an enhancement in the rate of disintegration of organic compound leading to low PAHs concentration.

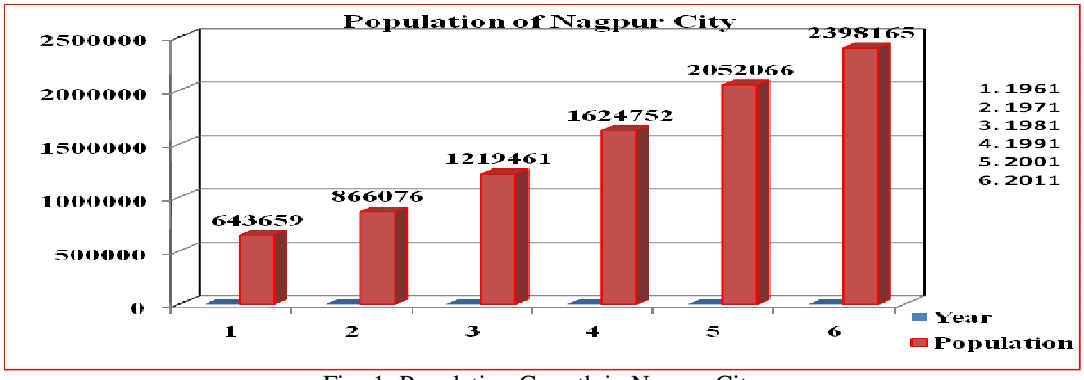


Fig.-1: Population Growth in Nagpur City

Secondly, the PAHs compounds are adsorbed/absorbed specially on <10 µ size particles. During summers, heavy dust storms is a climatic characteristic of Nagpur city which help to increase the Suspended Particulate Matter (SPM, >10µ size) concentration due to natural process. Low value of PAHs

in monsoon may be due to the less particle density during rainy reason hence chances for particle bound PAHs are also less[8].

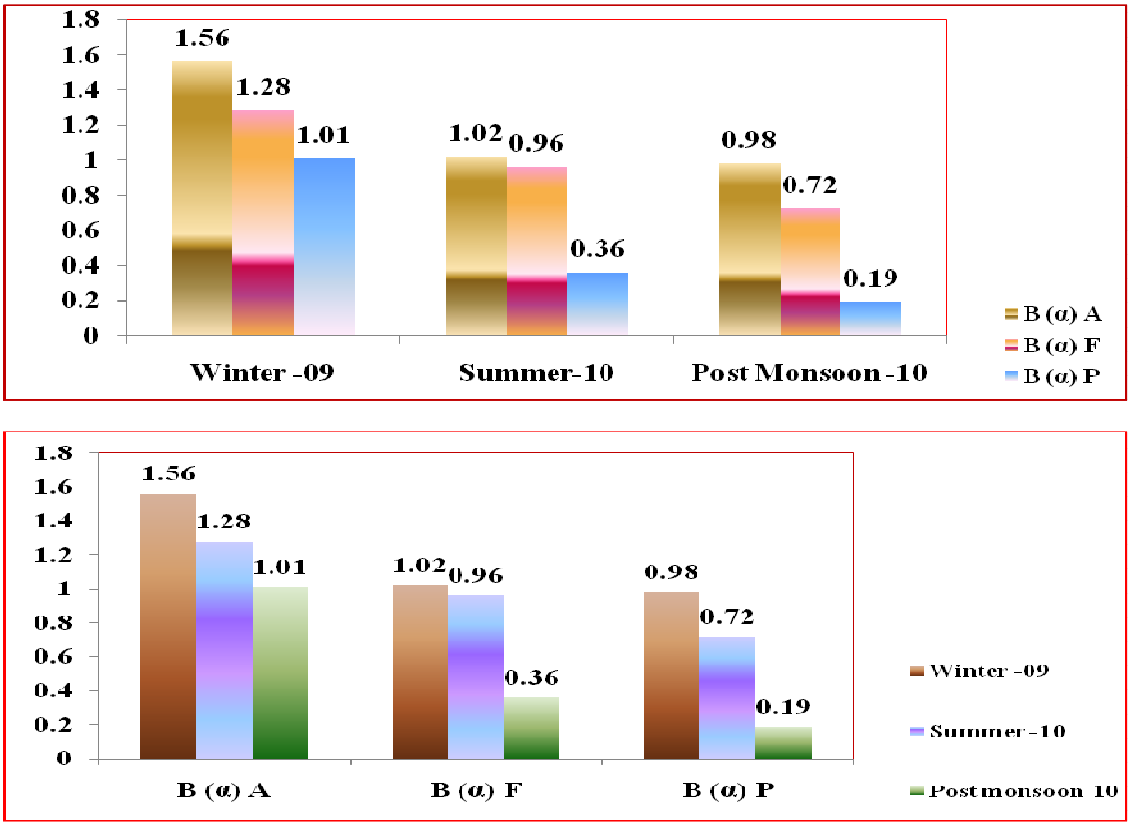


Fig.-2: Seasonal variation in PAHs concentration during session 2009-2010

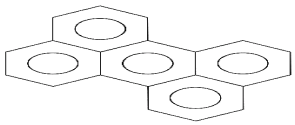
The results obtained during the study course reveal the presence of PAHs compounds in the ambient air of Nagpur city. Higher concentration observed in winter at commercial areas & minimum at residential area. This may be due to enhancement in the rate of disintegration of organic compound in summer. In summer heavy dust storm results in increase of SPM (10 µ size) but PAHs adsorbed specially on particle size less than 10µ which may also responsible for low PAHs concentration in summer. The presence of PAHs in ambient air of Nagpur city necessitates the continuous/regular monitoring of ambient air in the urban sector with respect to PAHs as this compound recognized as a very important factor in field of air pollution problem because of its carcinogenic nature[9].

CONCLUSION

As per the qualitative and quantitative analysis of PAHs in air samples, it may be concluded that qualitatively, the PAHs, such as B(α)A [Benzo Alpha Anthracene], B(α)F [Benzo Alpha Florescence] and B(α)P[Benzo Alpha Pyrene] were present in the air environment of study area i.e. Nagpur City (Table-7). Furthermore, on the basis of the data regarding seasonal variation of PAHs concentration in air, it may be concluded that a significantly ($P<0.05$) higher concentration of all the PAHs was prevalent during the winter season (Fig 2).

Anthracene by far the most abundant PAH in the whole ecosystem Most PAHs derived from biomass or fossil fuel combustion and is distributed in the atmosphere. Numerous local biological sources of PAHs are present; more research is needed in the area. Similarity in patterns to temperate regions.

Anthracene



Perylene

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