Studies on presence of PAHs in ambient air of Gwalior city

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ABSTRACT: 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) Fluoranthene [B{b}F] and Benzo (a) Pyrene [B(a)P] are known to be potentially weak, and moderate carcinogenic for this study. This report presents the profile of PAH, monitored in the particle bound ambient air of Gwalior region in Madhya Pradesh. High Volume 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 "BDL" to 156ng/m3, B(b)F concentration ranging from "BDL" to 128 ng/m3 and B(a)P was ranged from "BDL" to 101 ng/m3. 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. @ JASEM

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 substantially in 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 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.

In general, any organic compound containing two or more aromatic rings may be considered to be a polycyclic organic matter. The term "Poly cyclic aromatic hydrocarbon" commonly refers to a large class of organic compounds containing two or more fused aromatic rings made up of carbon and hydrogen atoms. At ambient temperature, PAHs are solids. The general characteristic common to the class are 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, sulfuric acid, ozone and hydroxyl radicals.

The PAHs principally are used as intermediate in the production of PVC’s & Plasticizers (naphthalene), Pigments (acenaphthene, pyrene), dyes (anthracene, fluoranthene), and pesticides (Phenethereone). The largest emissions of PAHs result from incomplete combustion of organic materials during industrial processes and other human activities including.

(i) Processing of coal, crude oil and natural gas, petroleum refining and production of carbon blacks, creosol & coal tar.
(ii) Aluminum, iron and steel production in plants and foundries.
(iii) Heating in power plants and residences and cooking.
(iv) Combustion of refuse.
(v) Motor vehicle traffic and
(vi) 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 processes. PAHs are photo oxidized in air and water in the presence of sensitizing radicals like OH, NO3 and O3. PAHs are
ubiquitous in the environment and various individual PAHs have been detected in different compartments 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 (Mukerjee et. al. 1989). 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 & gut of mammals to metabolize rapidly absorb them. The increase in pollution level of these compounds will increase the possibility of cancer patients (Thakur et. al. 1997). In biota, uptake processes for PAHs are related to their hydrophobic character. Due to above environmental significance, ambient PAHs concentration scenario has been elaborated and M.P. Pollution Control Board include Gwalior region for PAHs study from April 2001 to March 2002 which is one of the most growing city of Central India.

**MATERIAL AND METHODS**

**STUDY AREA**

Gwalior is located at northern part of Madhya Pradesh. The district is well connected by Road &NH-3, NH-75 and Railway Network. The main locations of the district are Morar, Pichhor, Dabra and Bhitarwar. The major reservoir of the district is Harsi. Gwalior is one of the important historical places of Madhya Pradesh. The Gwalior is blessed with Classical Music Maestro Miya Tansen. At Gwalior, the Gwalior Trade Fair take places every year in the month of December-January. The Tomars, Marwahs and Marathas ruled the Gwalior City. The modern area of Gwalior called Lashkar. Lashkar is few miles South from the old city. It is the site of factories producing cotton, yarn, paint, ceramics, chemicals, and leather products. The Jiwaji University was built in Gwalior in the year 1964. Gwalior City was the Capital of the princely State of Gwalior until 1948 and the summer Capital of Madhya Bharat State from 1948 to 1956. When Madhya Bharat became part of Madhya Pradesh, it becomes separate District. According to Census 2001, population of the District was 1629881. The sampling sites were selected on the basis of major activity at Maharajpura Industrial Area (I), Darpan Colony(R), Roxy Bridge(C), JC Mills Industrial Area (I), Morar(R), Phool Bagh (C), Madhav Nagar (R), Hazier (C), and Railway Station (C) represented/covered all Industrial, Commercial & Residential zones. To understand the extent of exposure of PAHs to urban population, routine monitoring of these compounds has been under taken in the city.

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 (Hoffman et. al, 1968) were selected for this study.

**SAMPLING**

The samples 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 pm to 10.00 pm  
(c) 10.00 pm to 6.00 am

by a High Volume Air Sampler (HVS) at a average rate of 1.2 m3/min.once in a month at each station from April-2001 to march 2002. The dust collected was used as the basic 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.

**SAMPLE PREPARATION**

Suspended particulates matter of diameter >10 µm and <10 µm were collected by High volume sampler and respirable dust sampler respectively on pre weighed glass fiber filter paper. After sampling glass fiber filter paper was put in envelope with care and transported to the Research Centre of M.P. Pollution Control Board, Bhopal for further analysis. The filter papers were 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 vessel for 6 hrs. using 100 ml cyclohexane in evaporating flask. After extraction, extract was reduced initially with the help of rotary evaporator up to 5 ml and then finally with nitrogen upto 1 ml. If the extract was clear, cleanup was not necessary. Now the sample was ready for Gas Chromatographic analysis by the method described by Lodge, 1989.

**CAPILLARY GAS CHROMATOGRAPHY**

Analysis of PAHs compounds has been performed by capillary Gas Chromatograph as described by Liberty et.al. 1964. For PAHs analysis, sigma 2000 (Perkin Elmer make) Gas Chromatograph with flame ionization detector (FID) was used. The analysis was carried out under the following experimental conditions.
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Column : (5%-phenyl) methyl polysiloxane, 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 upto 140° C for 0 min.
@ 10° C up to 290°C for 15 min.
Detector Temp.: 300 °C
Injector Temp. : 275 °C

**Instrumental Analysis:** Standardization was done using USA made Poly Science standards. Volume of injection was 2 µl and split open after 1 min. of injection. The identification and quantification of sample chromatograms with standard chromatograms were performed automatically by PE NELSON (Perkin Elmer) integrator; chromatograms were also checked manually by overlaying the standard and sample chromatograms.

**RESULTS AND DISCUSSIONS**
Trend of analysis of criteria pollutant (SPM) of Gwalior city is projected in (Table-I & II). Air quality status of SPM in Gwalior shows that average concentration of SPM is higher in commercial area followed by industrial area in 2001-2002. The SPM concentration levels in ambient air are reported minimum 69.44 µg/m³ at residential area and maximum 1645.5 µg/m³ at commercial area of Gwalior city. PAHs trend of Gwalior city on min-max basis projects that all the monitored PAHs are present in ambient air during 2001-2002 period. Out of three PAH compound B(a)A show highest concentration ranging from BDL to 156 ng/m³ followed by B(b)F varying from BDL to 128 ng/m³ and B(a)P from BDL to 101 ng/m³ (Table – III).

The seasonal variation of ambient PAHs level shows that the min-max concentration of B(a)A , B(b)F and B(a)P higher in winter as compared to other seasons, (Table – IV). 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. Secondly, the PAHs compounds are adsorbed/absorbed specially on <10 µ size particles. During summers, heavy dust storms is a climatic characteristic of Gwalior city which help to increase the 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.

**CONCLUSION**
The results obtained during the study course reveal the presence of PAHs compounds in the ambient air of Gwalior 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 Gwalior necessitates the continuous/regular monitoring of ambient air in the urban sector w.r.t. PAHs as this compound recognized as a very important factor in field of air pollution problem because of its carcinogenic nature.

<p>| Table I | Minimum-Maximum Ranges of SPM in Gwaior City (2001-2002) |</p>
<table>
<thead>
<tr>
<th>S. No</th>
<th>Area</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Industrial</td>
<td>110.5 (Maharajpura)</td>
<td>591.31 (Maharajpura)</td>
</tr>
<tr>
<td>2.</td>
<td>Commercial</td>
<td>106.6 (Hazira)</td>
<td>1645.5 (Phoolbagh)</td>
</tr>
<tr>
<td>3.</td>
<td>Residential</td>
<td>69.44 (Darpan Colony)</td>
<td>590.2 (Madhav Nagar)</td>
</tr>
</tbody>
</table>

* All results in µg/m³

<p>| Table II | Seasonal Concentration profile of SPM in Gwaior City (2001-2002) |</p>
<table>
<thead>
<tr>
<th>S. No</th>
<th>Area</th>
<th>Winter</th>
<th>Summer</th>
<th>Monsoon</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Industrial</td>
<td>167.85 – 247.37</td>
<td>363.63 – 591.39</td>
<td>110.5 – 399.0</td>
</tr>
<tr>
<td>2.</td>
<td>Commercial</td>
<td>315.7 – 1764.32</td>
<td>187.5 – 1136.6</td>
<td>106.6 – 771.9</td>
</tr>
<tr>
<td>3.</td>
<td>Residential</td>
<td>176.34 – 604.8</td>
<td>69.44 – 307.21</td>
<td>112.9 – 590.2</td>
</tr>
</tbody>
</table>

*All results in µg/m³

<p>| Table III | Minimum-Maximum Concentration of PAH's in Ambient Air of Gwalior Region (2001-2002) |</p>
<table>
<thead>
<tr>
<th>S. No</th>
<th>PAHs</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>B(a)A</td>
<td>Not Detectable</td>
<td>156</td>
<td>At Phoolbagh (C/W)</td>
</tr>
<tr>
<td>2.</td>
<td>B(b)F</td>
<td>Not Detectable</td>
<td>128</td>
<td>At Phoolbagh (C/W)</td>
</tr>
<tr>
<td>3.</td>
<td>B(a)P</td>
<td>Not Detectable</td>
<td>101</td>
<td>At Phoolbagh (C/W)</td>
</tr>
</tbody>
</table>

* All results in ng/m³

* C/W : Commercial/ Winter

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Table IV

<table>
<thead>
<tr>
<th>S. No</th>
<th>PAHs</th>
<th>Winter</th>
<th>Summer</th>
<th>Monsoon</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>[B(b)F]</td>
<td>ND - 128</td>
<td>ND - 96</td>
<td>ND - 72</td>
</tr>
</tbody>
</table>

*All results in ng/m³, *ND: Not Detectable

LIMITS FOR PAH’s
- OSHA (Occupational Safety & Health Administration)
  - 0.2 mg/cu mtr (for ambient air)
- NIOSH (National Institute for Occupational Safety & Health)
  - 0.1 mg/cu. mtr. For 10 hrs (for Human exposure)
- EU: 5 ng/m³ BaP (Annual Average)
- USA: 0.3 – 0.7 ng/m³ (Annual Average)
- GERMANY: 1.3 ng/m³ BaP (Annual Average)

REFERENCES


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