



# Comparative Estimation of Particulate Bound Polycyclic Aromatic Hydrocarbons: Trends at Industrial and Rural Areas of Visakhapatnam, India

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## Abstract

US-EPA listed 16 priority polycyclic aromatic hydrocarbons (PAHs) were characterized from the particulate matter samples ( $PM_{10}$ ) collected from two locations at Visakhapatnam, India during April 2011 to March 2012. The samples were collected from an industrial and a rural site using a high volume sampler. The samples were extracted with *n*-hexane and analysis was carried out with HPLC/UV-VIS detector. The annual total PAHs concentrations in  $PM_{10}$  at industrial site ranged from 19.4 – 95.5  $ngm^{-3}$  whereas at a rural site, it ranged from 7.8-36.8  $ngm^{-3}$ . The average total PAHs concentration at industrial site was about 2.4 times higher than that of the rural site. The monthly concentrations of total PAHs in  $PM_{10}$  at industrial site ranged between 20.9 – 90.1  $ngm^{-3}$  and it ranged from 9.4 - 35.8  $ngm^{-3}$  at rural site. The dominating PAHs at the industrial site were the high molecular weights PAHs while at rural site, the low molecular weight PAHs were dominant. The spatial variation in concentration of PAHs at two sites was mainly due to local emission sources. Significant correlation among comparative ring size PAHs showed their origin from similar sources. Potential sources of PAHs in  $PM_{10}$  were determined using the method of diagnostic ratios. The main sources contributing to PAHs at Industrial site were fossil fuel combustion and vehicular emission. At Rural site the potent sources contributing to PAHs were grass and wood combustion and vehicular emission, especially diesel and gasoline powered vehicles. Carcinogenicity of PAHs in terms of B(a)P equivalent concentration was found to be 3.1  $ngm^{-3}$  and 1.1  $ngm^{-3}$  for industrial and rural site, respectively.

**Keywords:** Polycyclic aromatic hydrocarbons (PAHs), spatial variation, diagnostic ratios, TEF.

## Introduction

The population growth, urbanization and various industrial activities lead to increased levels of pollutants in developing cities. The studies of these various pollutants in environment are carried out worldwide such as volatile organic compounds (VOCs) like benzene, toluene and xylene in atmosphere; pharmaceuticals in air; trace elements in soils and tomato leaves; and fruits and trace metal in fish parts<sup>1-4</sup> etc. Polycyclic aromatic hydrocarbons (PAHs) are a large group of VOCs which are fused ring structures containing carbon and hydrogen atoms. PAHs are declared as priority pollutants because of their carcinogenic and mutagenic properties<sup>5</sup>. PAHs have natural sources such as volcanic eruptions and forest fires. But mostly they are emitted through anthropogenic activities like cigarette and tobacco smoke, combustion processes related to energy generation, vehicular emission, industrial activities, domestic heating and incinerators<sup>6</sup>. At ambient temperatures, they can exist in particulate as well as in gaseous phase. Generally, PAHs with two or three aromatic rings in their structure generally exist in gaseous phase and PAHs with three or more aromatic rings remain associated with particulate phase.

Atmosphere is a major sink for distribution of PAHs. Once they

get released into the atmosphere, they get transferred to long distances. They show removal mechanisms from atmosphere such as oxidation and photolytic reactions<sup>5</sup> as well as wet and dry deposition<sup>7</sup>. PAHs are getting a large attention, because of their carcinogenic and mutagenic properties. Human exposure to PAHs leads to mutations, formation of DNA adducts, abnormal reproductive effects and also cancers of lung, skin, and urinary bladder. PAHs concentrations in ambient air have been studied in many cities of world. They mainly focus on the comparative study of various locations with different backgrounds. PAHs emitted from specific sources such as gasoline and diesel vehicle exhaust, domestic combustion and tobacco smoke have also been studied. It is observed that India is the second largest PAHs emitter in the world with an estimated total PAH emission of 90 Gg in 2004. In India, a lot of research on PAHs in different cities is published. For example, in Agra the average TPAHs concentrations were 97.93, 34.65, 28.67 and 8.04 $ngm^{-3}$  for the industrial, residential, roadside and agricultural sites, respectively<sup>8</sup>. In Ahmadabad, studies showed that total PAH concentrations ranged between 90–195  $ngm^{-3}$  at the industrial area whereas it ranged between 23–66  $ngm^{-3}$  at a residential area<sup>9</sup>. In Mumbai, the total PAH concentration was 38.8  $ngm^{-3}$  at an industrial cum heavy traffic area and it was 24.5  $ngm^{-3}$  at residential area<sup>10</sup>. In Tiruchirappalli, the total

PAHs concentrations at four sampling stations were 333.7, 202.6, 265.9 and 232.7 $\mu\text{g m}^{-3}$ , respectively<sup>11</sup>.

In present study, air particulate samples were collected from an industrial and a rural area of Vishakhapatnam, India. The samples were chemically processed and analyzed for their polycyclic aromatic hydrocarbons content using HPLC. Comparative assessment of the annual PAHs trends at these two sites was performed.

## Material and Methods

**Sampling site and Sample collection:** Among the Indian metropolitan cities, Visakhapatnam (Latitude 17° 42' 81" N, Longitude 83° 18' 42" E), is the second largest city in the state of Andhra Pradesh. It has geographical importance in India as the only natural harbor on the east coast. A large industrial and commercial area is developed in the city such as NTPC, Visakhapatnam Steel Plant, HPCL, Bharat Heavy Plates and Vessels Limited, Jawahar Nehru pharma city and Coromondal fertilizer etc. The harbor is also an input of pollutants like crude oil, iron ore and sulfur dust spilled during loading and unloading operations. The transportation in the city is mainly road based. For the city, air pollution studies are carried out at different parts like commercial, heavy traffic and densely populated sites which revealed high levels of SPM, NO<sub>2</sub> and SO<sub>2</sub> in ambient air. But in Vizag, a very limited data is available on concentration of PAHs. So, the aim of present paper is to study the concentration levels, spatial variation with emphasis on possible potent carcinogenicity of atmospheric PAHs at Visakhapatnam.

In present study, PM<sub>10</sub> samples were collected from two different locations at Visakhapatnam. The first location is at "Paravada" which is a representative of typical industrial site with few residences. It is surrounded by various industries and it is nearby national highway which is 8 km away from it. It has a direct impact of industrial emissions, vehicular traffic and household burning activities. The second sampling location is at

"Atchutapuram" which is a densely populated rural residential site. This area is 18 km away from the national highway. At this location, combustion activities like biomass burning through cooking and farming were observed. Figure-1 shows the sampling sites in Visakhapatnam. PM<sub>10</sub> samples were collected during April 2011 to March 2012. Envirotech Respirable high volume sampler and glass fiber filter papers were used for sampling. PM<sub>10</sub> samples were collected twice a week with flow rate of 1.1 m<sup>3</sup> min<sup>-1</sup>. After sampling, the filter papers were handled carefully and kept at cool place till extraction procedure.

**Extraction and Analysis of PAHs:** One fourth portion of filter paper was chopped into pieces and taken in 50ml conical flask. About 30 ml of HPLC grade n-hexane (by Merck) was added into it and samples were extracted with ultrasonic method for 1h. Then the extracts were filtered through a pre-hexane washed Whatman 542 filter paper and then a cleanup process was carried out. The filtered extract was passed through a column filled with slurry of silica gel. The desired PAHs fraction was eluted with n-hexane and it was concentrated by passing gentle stream of ultra-pure nitrogen.

The analysis of the extracts was carried out for 16 US-EPA priority PAHs. The environmental samples are highly complex. So it is important that the analytical method used should be capable of reasonable separation of peaks of analyte of interest especially when analytes are composed of several isomers<sup>12</sup>. Hence, HPLC (high performance liquid chromatography) system supplied by Shimadzu, LC-10 AD, Japan with UV-VIS detector set at 254 nm was used for analysis of 16 PAHs. In this system, main column (length 250 mm) and a guard column (length 10 mm) with 4.6 mm inner diameter are provided. Both are loaded with round RP-18 material for better separation. For mobile phase, mixture of Acetonitrile (88%):water(12%) was used in isocratic mode at the rate of 0.85 ml/min. The output of the detector was connected to chromatography workstation "Jasco-Borwin".

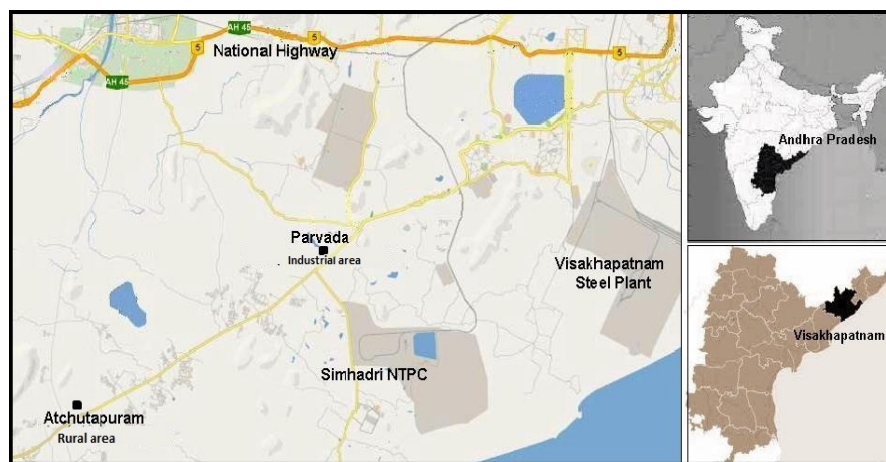


Figure-1  
Map showing sampling locations at Industrial and Rural sites in Visakhapatnam

**Quality control:** After 24 h sampling, all the filter papers were stored at 4°C and analyzed within 15 days from the date of collection. Field blank filter papers were collected to reduce the gravimetric error during sampling and filter paper handling. Quantification of PAHs was carried out by comparing the retention times and the peak areas of the samples with standards. PAHs standards supplied by Supelco, USA, dissolved in HPLC grade Acetonitrile were used for determining the retention data and for studying the linearity of the detector. To determine the limit of detection, serial dilutions of the PAHs standard were run and it was found in the range of 0.007 to 0.016 ng for the different compounds. 16 PAHs compounds including Naphthalene [Naph], Acenaphthylene [Acy], Acenaphthene [Ace], Fluorene [Fluo], Phenanthrene [Phen], Anthracene [Anth], Fluoranthene [Flt], Pyrene [Pyr], Benzo (a) Anthracene [B(a)A], Chrysene [Chry], Benzo(b) Fluoranthene [B(b)F], Perylene [Pery], Benzo(k) Fluoranthene [B(k)F], Benzo (a) Pyrene [B(a)P], Benzo (ghi) Perylene [B(ghi)P], Indeno (1,2,3- cd) Pyrene [IP] were analyzed<sup>13</sup>.

## Results and Discussion

### Concentrations levels of PAHs at Industrial and Rural sites:

Table-1 represents the annual average (AVG), minimum (MIN), maximum (MAX) and standard deviation (SD) of concentrations of PAHs measured in the PM<sub>10</sub> at Industrial and rural sites in Visakhapatnam during March 2011 to February 2012. Annual TPAHs concentration at industrial site varied between 19.4 ngm<sup>-3</sup> to 95.5ngm<sup>-3</sup> with an average concentration of 52.5ngm<sup>-3</sup>. At rural site, TPAHs concentration varied between 7.8ngm<sup>-3</sup> to 36.8ngm<sup>-3</sup> with an average of 21.7ngm<sup>-3</sup>. Throughout the study period, lots of fluctuations in concentration levels of PAHs were observed which may be generally due to the meteorological conditions and the different

local sources of PAHs at the sampling locations.

At industrial site, the concentrations of individual PAH ranged between 0.1-18.6 ngm<sup>-3</sup> and significant higher level of Acy, Fluo, Phen and Ace were observed. The concentration of Benzo(a)Pyrene, which is most potent carcinogen among the PAH compounds, was found to be in the range of 0.4 - 4.1 ngm<sup>-3</sup>. Also, significant concentrations of B(ghi)P, Pyr, B(k)F and B(b)F were observed. At rural site, the concentrations of individual PAH ranged between 0.1-8.2 ngm<sup>-3</sup> and high concentration levels of Naph, Acy, Phen, Pery and B(ghi)P were observed. The concentration of Benzo(a)Pyrene, ranged between 0.2 - 1.1 ngm<sup>-3</sup>.

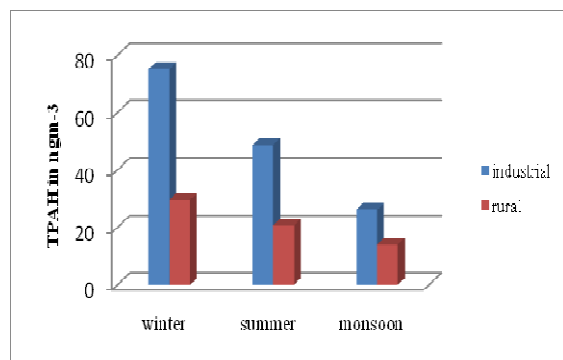
**Spatial variations of PAHs:** A significant spatial variation was observed at the two sampling locations (table 1). The average concentrations of PAHs in PM<sub>10</sub> at industrial site were much higher than that at the rural site. At Industrial site, maximum TPAH concentration was observed in month of January (90.1 ngm<sup>-3</sup>) and minimum TPAH concentration was observed in month of August. At Rural site, maximum TPAH concentration was observed in month of January (35.8 ngm<sup>-3</sup>) and minimum TPAH concentration was observed in month of September (9.4 ngm<sup>-3</sup>). The TPAH concentration in January at industrial site was 2.5 times higher than that of the rural site. The annual average TPAH concentration at industrial site was 2.4 times higher than the average annual TPAH concentration at rural site. Similarly, when the seasonal data between two sites was compared, it showed that TPAH concentrations in winter, summer and monsoon at industrial site were more than twice than that of the rural site. Figure-2a shows the annual average concentrations of total PAH (in ngm<sup>-3</sup>) in winter, summer and monsoon at industrial and rural sites.

Table-1

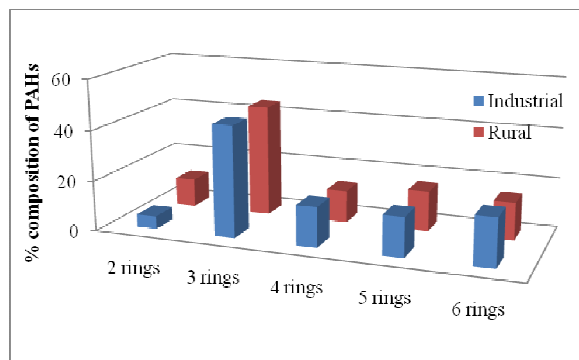
The annual average concentrations (AVG), minimum (MIN), maximum (MAX) and standard deviation (SD) of individual PAH (in ngm<sup>-3</sup>) in PM<sub>10</sub> at Paravada (Industrial site) and Atchutapuram (Rural site)

Pah	Industrial site				Rural site			
	Min	Max	Avg	Sd	Min	Max	Avg	SD
Naph	0.7	5.6	2.7	1.3	0.8	5.5	2.5	1.2
Acy	3.6	18.6	11.9	4.2	1.0	8.2	4.2	1.7
Fluo	1.5	7.5	3.5	1.5	0.1	2.9	1.6	0.6
Ace+ Phen	1.0	8.1	4.0	1.7	0.8	4.6	2.3	1.0
Anth	1.0	7.6	3.8	1.8	0.3	2.9	1.6	0.6
Flt	0.7	3.6	1.8	0.8	0.1	2.8	0.8	0.7
Pyr	1.0	9.5	4.2	2.4	0.2	1.9	0.9	0.4
Chry+ BaA	0.6	4.2	2.4	1.0	0.2	2.6	1.1	0.6
B(b)F	0.3	3.9	1.8	1.0	0.2	2.1	0.8	0.4
B(k)F	0.4	7.8	2.9	1.8	0.4	2.1	0.9	0.4
Pery	0.1	3.9	1.4	1.1	0.5	2.5	1.1	0.4
B(a)P	0.4	4.1	2.1	1.0	0.2	1.1	0.7	0.3
IP	0.3	5.4	2.1	1.2	0.2	2.1	0.8	0.4
BghiP	2.4	17.6	8.0	4.8	0.9	5.3	2.5	1.3

PAHs with molecular weight <252 are known as low molecular weight PAHs (i.e. 2 and 3 rings PAH) which generally tend to remain in vapor phase. PAHs with molecular weight >252 are known as high molecular weight PAHs (i.e. 4, 5 and 6 rings PAHs) and they tend to remain in particulate phase as they have low vapor pressure. Figure-2b shows the percentage composition of PAHs having different number of Benzene Rings at two different locations in Visakhapatnam. At industrial site, the percentage concentration of LMW PAHs was around 49% of total PAHs mass and the percentage of HMW PAHs was 51%. At rural site, the LMW PAHs contributed around 56% of the total PAHs mass and the percentage of HMW PAHs was 44%.



**Figure-2a**  
 Annual average concentrations of total PAH (ngm<sup>-3</sup>)



**Figure-2b**  
 Percentage composition of aromatic ring wise PAHs at industrial and rural site

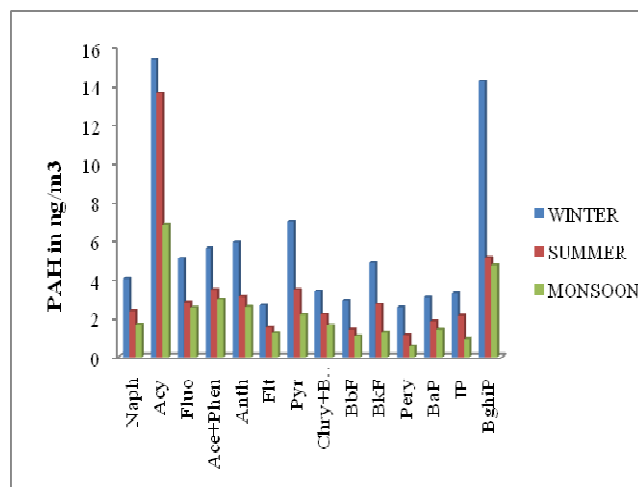
The reason for this variation could be the peculiar location of sampling sites with different local sources of PAHs. The sampling location at Parvada is surrounded by industries and very near to a highway. So this site is exposed to high levels of PAHs emitted through industrial emissions and vehicular exhausts<sup>14</sup>. Also, levels of PAHs in the ambient environment depend upon variety of combustion processes, type of fuel and combustion temperature etc<sup>15</sup>. On the other side, other sampling location at Atchutapuram is a rural site, away from the industrial area. Therefore, here the major sources of PAHs could be household cooking activities and other burning activities with

low volume of vehicular exhaust.

**Seasonal variations of PAHs:** Visakhapatnam has tropical type of climate with excessive humidity due to proximity of Bay of Bengal. The summer season is observed from March to June when the temperature is around 45°C. The monsoon season is from July to October with irregular but heavy showers. During the study period, the annual average rainfall of 95 centimeters was observed. The winter season is from November to February with average temperature of 25°C.

During seasonal study of PAHs, significant variation in concentrations of PAH was observed. The average values of individual PAH concentration in PM<sub>10</sub> in winter; summer and monsoon at the two sites are presented in Figure-3. The study revealed that the concentrations of 16 PAHs in winter were higher than that in summer and in monsoon at both sites. It was in agreement with earlier studies where the concentrations of particle associated PAHs in urban areas were higher in winter than summer<sup>16,17</sup>. At industrial site, the TPAH concentration in winter (79.9 ngm<sup>-3</sup>) was about 2.5 times higher than that of the monsoon (31.6ngm<sup>-3</sup>). Acy, Ace, Phen, Pyr, BkF and BghiP showed higher concentrations in winter. The TPAH concentration in summer was 46.9 ngm<sup>-3</sup>. At rural site, the TPAH concentration in winter (31.7ngm<sup>-3</sup>) was found to be more than twice than that of the TPAH concentration in monsoon (14.4ngm<sup>-3</sup>) with higher concentrations of Acy, Ace, Phen, Chry, BaA and BghiP. The TPAH concentration in summer was found to be 19.5 ngm<sup>-3</sup>.

The concentrations of PAHs were found high in winter were due to prevailing meteorological conditions. In winter, wind speeds are slow and the atmosphere is cold. This controls the dispersion of pollutants, results in higher concentration of PAHs in winter. In summer,



**Figure-3a**  
 The seasonal variation of average concentrations of PAHs (in ngm<sup>-3</sup>) at Industrial site

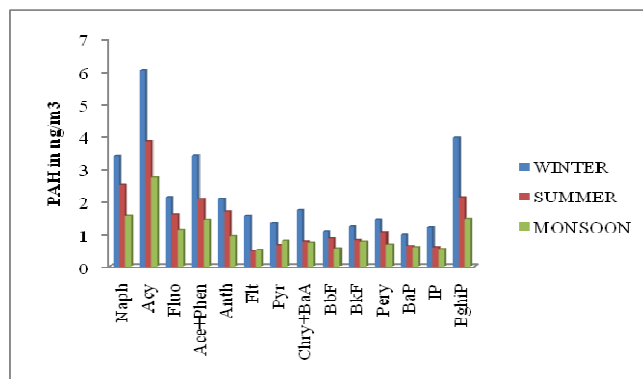


Figure-3b

**The seasonal variation of average concentrations of PAHs (in ngm<sup>-3</sup>) at Rural site**

increased photodecomposition and high dispersion results in lower concentrations of PAHs. In monsoon, the least PAHs concentrations were observed due to the precipitation as compare to summer<sup>18</sup>. The PAHs concentrations are also affected by meteorological parameters like temperature, rainfall and wind directions. Moreover, the high PAHs concentrations in winter were also because of the local sources like cold start of engines, burning of crops and increase in use of fuels during domestic activities etc<sup>16</sup>.

**Correlation studies:** It can be assumed that two or more components may correlate with each other if they have a common origin or surrounding conditions<sup>19</sup>. Hence, correlations among PAHs are studied using Univariate Pearson correlation to determine their probable sources. Table-2 represents the correlation matrix between PAHs at industrial site. The values >0.5 show significant correlation between the two variables. At industrial site, good correlations for the LMW PAH like Fluo, Acy, Ace, Phen and Anth was observed which can be indicative of stationary sources that is nearby the site such as steel industry or thermal power plant<sup>10,16</sup>. Also, significant correlation was observed among HMW PAH such as Pyr, BkF and BghiP and among BkF, IP, BaA and Chry. These PAHs indicate their origin from gasoline and diesel combustion<sup>15</sup>.

Table-3 represents the correlation matrix between PAHs compounds at rural site. At rural site, significant correlation was obtained among the LMW and HMW PAHs like Acy and Ace, Phen, Pery IP, BghiP. Good correlation was observed among Anth and Ace, Phen, IP and BghiP. It is indicative of combustion activities like vehicular emission. Significant correlation among HMW PAH such as BkF, Pyr, BaA, Chry and BaP points the wood combustion<sup>15,19</sup>. Also good correlation was seen among Pyr, BkF, IP, and BghiP which indicates the gasoline and diesel burnings. The significant correlation among Bap, IP and BghiP showed biomass burning like wood, dung cake burning activities<sup>10</sup>.

**Diagnostic ratios of PAHs:** Molecular diagnostic ratio of PAHs

is a reliable technique to identify the potent sources of PAHs. PAHs from different combustion sources have significant variation in their composition and their fingerprints can be used in the source identification<sup>20</sup>. Table-4 shows the values of diagnostic ratios of PAHs in present study and signature values given in literature. It showed that the ratio IP/ (IP+BghiP) has value of 0.2 at industrial site, which is similar to that of petrogenic combustion. The value for same ratio at rural area was 0.24 which is reported for petroleum product combustion<sup>21</sup>. Fluo/(Fluo+Pyr) ratio showed the value 0.48 at industrial site which indicates fossil fuel combustion like coal (in the range of 0.4-0.5) and it was 0.64 at rural site which indicated grass and wood combustion<sup>22</sup>. The values 0.28 and 0.31 were obtained for the ratio IP/B(ghi)P for industrial and rural site, respectively which are signature of gasoline engine<sup>23</sup>. BaP/BghiP ratio had the value 0.29 at industrial site. It ranged between 0.2-0.4 which is reported for gasoline engine<sup>23</sup>. At rural site this ratio was 0.31 which is reported for vehicular emission<sup>24</sup>. The value for BbF/BkF ratio was >0.5 at both the sites which may attribute to diesel emissions<sup>17</sup>. The value for ratio Flt/Flt+Pyr was observed 0.31 at industrial site which indicates petroleum source and it was 0.43 at rural site, which indicates gasoline engine<sup>17,21</sup>. Thus, the diagnostic ratio studies showed that the important source of PAHs in Visakhapatnam was gasoline and diesel powered vehicles. Along with this, petrol emission was also observed at industrial site which is near highway. At rural site, grass and wood combustion was observed which are used for cooking in a rural residential area.

**PAH exposure profiles and TEFs of PAHs:** The occupational exposure limit for PAHs has not been yet established because of the complications of structures of PAHs and their chemical composition. Benzo (a) pyrene is considered as most carcinogenic PAH and studies have proved that BaP is mutagenic for human cells in culture as well as carcinogenic in animals. Hence, the impact of PAH on health can be determined by the toxic equivalency factor (TEF) after the PAH concentration is converted to a BaP equivalent concentration (BaPeq)<sup>25</sup>. The toxic equivalent factor (BaPeq) of a given PAH compound can be calculated by multiplying the concentrations of PAHs by its value of TEF. To calculate the TEF in present study, the values given by Nisbet and Lagoy were used. Table-5 presents the average concentration of PAHs corresponding to BaP equivalent factors at industrial and rural sites in Visakhapatnam.

The average TPAH at industrial site was 51.06 ngm<sup>-3</sup>, which corresponds to BaPeq concentration of 3.1 ngm<sup>-3</sup>. The highest BaPeq concentration was contributed by BaP and it was 66.4% followed by BkF (9%), Chry+BaA (7.6%) and IP (7%). The average TPAH at rural site was 20.67 ngm<sup>-3</sup>, which corresponds to BaPeq concentration of 1.12 ngm<sup>-3</sup>. The contribution of BaP was 63% in terms of carcinogenicity followed by Chry+BaA (10%), BkF (8%) and BbF (7%). The dominant PAHs in PM<sub>10</sub>

**Table-2**  
**Correlation matrix between PAHs compounds at industrial site**

	Naph	Acy	Fluo	Ace+Phen	Anth	Flt	Pyr	BaA+Chry	BbF	BkF	Pery	BaP	IP	BghiP
Naph	1													
Acy	0.367	1												
Fluo	0.25	0.557*	1											
Ace+Phen	0.234	0.654**	0.571*	1										
Anth	0.271	0.648**	0.274	-0	1									
Flt	0.29	0.347	0.27	0.15	0.340	1								
Pyr	0.337*	0.42	0.182	-0.1	0.420	0.339	1							
BaA+Chry	0.537*	0.242	0.216	0.155	0.330	0.360	0.488	1						
BbF	0.355	0.471	0.412*	0.152	0.340	0.463	0.511	0.442	1					
BkF	0.370*	0.559**	0.356*	-0.15	0.460	0.369	0.702**	0.505*	0.540	1				
Pery	0.265	0.492	0.344*	0.222	0.240	0.377	0.394	0.292	0.390	0.399*	1			
BaP	0.324	0.339	0.146	0.13	0.150	0.360	0.486*	0.333	0.450	0.320	0.430*	1		
IP	0.374*	0.577*	0.543*	0.189	0.460	0.367	0.434	0.518*	0.537	0.631*	0.336	0.245	1	
BghiP	0.356	0.345	0.261	-0.08	0.320	0.219	0.671*	0.475	0.477	0.776**	0.266	0.284	0.461*	1

\*Correlation is significant at the 0.05 level (2-tailed), \*\*Correlation is significant at the 0.01 level (2-tailed)

**Table-3**  
**Correlation matrix between PAHs compounds at rural site**

	Naph	Acy	Fluo	Ace+Phen	Anth	Flt	Pyr	BaA+Chry	BbF	BkF	Pery	BaP	IP	BghiP
Naph	1													
Acy	0.347	1												
Fluo	0.338*	0.574	1											
Ace+Phen	0.145	0.739**	0.460	1										
Anth	0.344	0.649**	0.493	0.651*	1									
Flt	0.120	0.639*	0.446	0.649*	0.434	1								
Pyr	0.066	0.561*	0.431	0.604	0.332	0.721**	1							
BaA+Chry	0.165	0.558	0.439	0.643*	0.429	0.698*	0.657*	1						
BbF	0.208*	0.597*	0.517	0.520	0.577	0.441	0.401	0.345	1					
BkF	0.241	0.611	0.418	0.561*	0.388	0.545	0.620*	0.544*	0.415*	1				
Pery	0.191	0.694*	0.473	0.646*	0.560	0.609*	0.443	0.445	0.537*	0.512	1			
BaP	0.112	0.593	0.418	0.697*	0.405	0.617	0.669*	0.698*	0.423	0.557	0.513	1		
IP	0.187	0.714**	0.466	0.747*	0.512	0.709**	0.635	0.656*	0.421	0.679*	0.676*	0.659*	1	
BghiP	0.320*	0.786**	0.558	0.738*	0.538	0.766**	0.742**	0.764*	0.551	0.737*	0.655*	0.698*	0.791**	1

\*Correlation is significant at the 0.05 level (2-tailed), \*\*Correlation is significant at the 0.01 level (2-tailed)

**Table-4**  
**Molecular diagnostic ratios of PAHs and their possible sources**

Dignostic Ratio	Industrial site			In Literature	Sources	References
	Min	Max	Mean	Mean/Range		
IP/ (IP+BghiP)	0.12	0.32	0.20	≤0.2	petrogenic source	21
Fluo/ (Fluo+Pyr)	0.37	0.62	0.48	0.4-0.5	fossil fuel combustion	22
IP/BghiP	0.13	0.46	0.28	0.2-0.4	gasoline engine	23
BaP/BghiP	0.16	0.44	0.29	0.2-0.4	gasoline engine	23
BbF/BkF	0.41	1.07	0.67	>0.5	Diesel emission	17
Flt/Flt+Pyr	0.25	0.39	0.31	< 0.4	Petroleum	17
Dignostic Ratio	Rural site			In Literature	Sources	References
	Min	Max	Mean	Mean/Range		
IP/ (IP+BghiP)	0.16	0.32	0.24	0.2 -0.5	Petroleum combustion	21
Fluo/ (Fluo+Pyr)	0.53	0.76	0.64	>0.5	grass, wood combustion	22
IP/BghiP	0.19	0.48	0.31	0.2-0.4	gasoline engine	23
BaP/BghiP	0.19	0.50	0.31	0.2-0.5	vehicular emission	24
BbF/BkF	0.52	1.26	0.88	>0.5	Diesel emission	17
Flt/Flt+Pyr	0.27	0.62	0.43	0.3-0.6	gasoline engine	17,21

**Table-5**  
**Average PAH concentration converted into BaPequ factors (in ngm<sup>-3</sup>) at industrial and rural sites at Visakhapatnam**

PAH	TEFs by Nisbet and LaGoy, 1992	AVG PAH at Industrial site	BaPequ conc at Industrial site	AVG PAH at Rural site	BaPequ conc at Rural site
Naph	0.001	2.68	0.0027	2.46	0.0025
Acy	0.001	11.86	0.0119	4.2	0.0042
Fluo	0.001	3.47	0.0035	1.6	0.0016
Ace+P hen	0.001	3.99	0.0040	2.28	0.0023
Anth	0.01	3.85	0.0385	1.56	0.0156
Flt	0.001	1.79	0.0018	0.85	0.0008
Pyr	0.001	4.18	0.0042	0.92	0.0009
Chry+ BaA	0.1	2.39	0.2387	1.07	0.1067
BbF	0.1	1.79	0.1788	0.83	0.0831
BkF	0.1	2.92	0.2920	0.93	0.0932
BaP	1	2.1	2.1006	0.71	0.7099
IP	0.1	2.08	0.2080	0.76	0.0764
BghiP	0.01	7.98	0.0798	2.5	0.0250
Total	-	51.06	3.16	20.67	1.12

were Acy, Fluo, Ace, were Acy, Fluo, Ace, Phen and BghiP with high concentrations at both the sites, but they actually contributed very less to the carcinogenic activity. Along with this, during winter the total BaP<sub>eq</sub> concentrations were found higher at both the sites and it was 3.2 ngm<sup>-3</sup> at industrial site whereas it was 1.2 ngm<sup>-3</sup> at rural site.

## Conclusions

The TPAHs concentrations were found higher at industrial site than the rural residential site. Annually, the total PAHs varied between 19.4 – 95.5 ngm<sup>-3</sup> at industrial site with average of 52.5 ngm<sup>-3</sup> and it varied between 7.8- 36.7 ngm<sup>-3</sup> with average of 21.7 ngm<sup>-3</sup> at rural site. Significant variation in concentrations of total PAHs throughout the study period was observed. The monthly concentrations of total PAHs in PM<sub>10</sub> at industrial site ranged between 20.9 – 90.1 ngm<sup>-3</sup> and it ranged from 9.4 - 35.8 ngm<sup>-3</sup> at rural site. The dominating PAHs at the industrial site were the high molecular weight PAHs which accounted for 51% of total PAHs while at rural site, low molecular weight PAHs were dominating which accounted for 56% of total PAHs. The winter concentrations of TPAHs were 2 to 2.5 times higher than monsoon concentrations at both the locations. The average total PAHs concentration at industrial site was about 2.4 times higher than that of the rural site. The spatial variations in concentrations of PAHs were observed due to different local sources of PAHs at sampling sites. PAHs with comparative ring sizes showed significant correlation with each other. It suggested a similarity both in their sources and in physico-chemical properties. The diagnostic ratios studies for source identification showed that the vehicular emissions including diesel and gasoline powered vehicles and fossil fuel combustion were the major sources of PAHs at industrial site while vehicular emissions and wood and grass burning were the major sources of PAHs at rural site, in Visakhapatnam. The BaP equivalent concentration was found to be 3.16 ngm<sup>-3</sup> at industrial site and 1.12 ngm<sup>-3</sup> at rural site.

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