Assessment of Source Profile of Non Methane Hydrocarbon in the Ambient Air of Metro City Delhi, India

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Abstract
In this paper presents the assessment of source profile of nonmethane hydrocarbons (NMHCs) in the ambient air of Delhi. The samples were collected from five different urban sites using tedlar bags for aliphatic NMHCs and activated adsorption charcoal tubes for aromatic NMHCs during October 2014 to September 2015. Eleven aliphatic NMHCs propane, n-butane i-butene, i-butane, 1,3-butadiene, trans-2-butene, cis-2-pentene, n-pentane, n-hexane, heptane and four aromatic NMHCs benzene, toluene, o-xylene, p/m-xylene were identified in 112 urban ambient air samples. Samples were analysed using gas chromatography which is coupled with flame ionization detector (GC-FID). Pearson correlation coefficient (r) found to be $0.5\pm0.2$, shows significance level to have moderate among the NMHCs, indicates NMHCs in the urban ambient air have many sources profile mentioned in PCA result. Factor analysis (FA) and receptor model, i.e., Principal Component Analysis (PCA)/Absolute Principal Component Score (APCS) was used for identification of source profile distribution. PCA analysis after the varimax rotation have identified six possible source profile and explained about 70% of the total data set. The average % contribution of NMHCs emitted from vehicles was found to be 23%, whereas polymer manufacturing industries contributes 19% and from refinery operation/gas station contribute 14%, and 13%, emitted from flare emissions and 10% from natural gas emissions. The secondary industrial process, including paints, body soaps and metal fabricator and processing was contributing 8%. Out of these remaining 13% was estimated as unidentified sources. These findings may be used by government authorities to formulate policies and strategies for improvement of urban air quality that can improve the health of urban communities.
Introduction
In the urban atmosphere non methane hydrocarbons (NMHCs) are most important groups of air pollutants. It is an important precursor of ground level ozone (O$_3$) and peroxy acyl nitrates (PAN) formation which can injurious to human health and vegetation. These NMHCs are emitted from both anthropogenic and natural sources in the ambient atmosphere. Thus, major anthropogenic sources are fossil fuel combustion automobile exhaust, industrial processes, liquefied petroleum gases (LPG) petroleum distillation and fuel evaporation and solvent use. Besides of anthropogenic sources, vegetation is the major contributors of biogenic NMHCs. For instance, isoprene is the most important biogenic source of NMHCs in the rural areas. Other sources of biogenic NMHCs includes oceanic emissions and those from microbial production. In the urban areas, NMHCs levels are largely govern by the various factors including motor vehicle type/ages, fuels used by the vehicles, flow rate, speed of traffic, road condition and human activities, seasonal variability and environmental conditions. However, emissions of aromatic organic hydrocarbons (i.e., aromatic, olefin and other organic compound) are increases by fuel used in the vehicles especially from without catalytic converter. For this, Liu et al. has reported that the gasoline fuel and automobile exhausts are the significant emitters of aromatic organic hydrocarbons. These aromatic hydrocarbons such as benzene, toluene and xylene isomers are present in abundant in the urban atmosphere. Among the aromatic hydrocarbons, xylene is considered the most reactivity as compared to ethyl benzene, although due to low reactivity and longer lifetime benzene is the most stable in the atmosphere. Tan et al. have been reported that the NMHCs are primarily emitted from vehicular emission except the aromatic hydrocarbons which mainly originated from solvent evaporation in the Foshan, China. On the other hand the major sink of NMHCs, are hydroxyl (OH) and nitrate radicals (NO$_3$) in the atmosphere. Additionally, halogen atom reactions are other important sink of NMHCs in the coastal areas.

PCA/APCS model have been more commonly used to the identification of possible source of NMHCs across the world. For example, Guo et al. applied PCA/APCS receptor model to the identification of possible sources of NMHCs and identified the vehicular exhausts and bio-fuel burning were the main source in eastern China. Sanchez et al. used PCA/APCS receptor model and they identified natural gas emissions was the major contributors of NMHCs whereas flare emissions, refinery process, fugitive gasoline emissions, industrial processes, and vehicle exhausts were lesser in number. For examples, NMHCs concentration was found to be higher in the refinery region in the Bombay city. Sahu and Lal have reported the concentration of lighter hydrocarbons were elevated because of vehicular emission, natural gas emission and leakage of liquid petroleum gas in the urban atmosphere of Ahmedabad city, India. Pandit et al. applied PCA receptor model on atmospheric NMHCs in Mumbai, India. They found vehicular emission was the major source of NMHCs.

In the Indian context concentration measurement of NMHCs and its source identifications are relatively fewer in number. For examples, NMHCs concentration was found to be higher in the refinery region in the Bombay city. Sahu and Lal, have reported the concentration of lighter hydrocarbons were elevated because of vehicular emission, natural gas emission and leakage of liquid petroleum gas in the urban atmosphere of Ahmedabad city, India. Pandit et al. applied PCA receptor model on atmospheric NMHCs in Mumbai, India. They found vehicular emission was the major source of NMHCs.

In the context of ambient air of Delhi, no comprehensive study has been reported on the concentration measurement and source apportionment of NMHCs species. Delhi is a industrial, commercial, educational, tourism and transportational hub and capital city of India. These above activities are to be increased pollution load in the ambient air and pertain grave environmental concern to the city dwellers. Therefore, the complete information on ambient levels of NMHCs is needed to develop a policies and strategies by the government authorities for improving the urban air quality and controlling ground level ozone formation. In the present study, we examined the concentration of selected NMHC and its source identification and percentage contribution using PCA/APCS receptor model in the metro city, Delhi, India.

Methodology
Sampling Location
Delhi is the capital territory of India surrounded by three sides of Haryana and Gangetic plains of Uttar Pradesh to the east. It is located in between the latitudes and longitude 28°20'0"N to 28°50'0"N and
longitude of 76°50'0"E to 77°20'0"E, respectively. Delhi climate is subtropical where continental air leads to dry conditions and extremely hot in the summer season. The Delhi monthly mean temperature varies from 14.3 °C in January to 34.5 °C in June, while the average annual temperature is 25.3 °C. In Delhi, winter is a most remarkable season which is starting from December and ending in February and cold air and ground based inversion are prevailing with low wind situation, i.e., less than one meter/second leads to frequently increase the concentration of pollutants).

Sampling
We have chosen two basic approaches for the sampling of NMHCs compounds, i.e., Tedlar bag and charcoal adsorption tube in the urban ambient air of metro city of Delhi. In the present study, for aliphatic NMHCs compounds propane, n-butane, iso-butane, trans-2-butane, iso-butene, 1,3-butadiene, iso-pentane, n-pentane, cis-2-pentene, n-hexane and n-heptane were collected with a pre-evacuated 2L Tedlar PLV sampling bag (CEL Scientific Corp. USA) using pump at the height of about 2m above the ground. Tedlar bags were flushed with ambient air and nitrogen gas prior to sampling of NMHCs compounds. Total 56 air samples (three sample in a week) were collected for measure of aliphatic NMHCs between 6.00 AM to 9.00 AM, Indian Standard Time (IST) at different characteristic site v.z., Income Tax Office (ITO) as traffic intersection, Mayapuri (MP) as an industrial site, Rohini (ROH) as residential and Jawaharlal Nehru University (JNU) as an urban background site. Simultaneously, total 56 air samples of aromatic NMHCs benzene, toluene, o-xylene and p/m-xylene were collected through charcoal adsorption ORBO™-32 tubes(O.D.xL 6mm), Supelco, Sigma Aldrich, India, using VOCs sampler. After sampling both ends of each ORBO™-32 tube was sealed with Teflon tape and wrapped with aluminium foil. These tubes were transferred to the laboratory and stored in the refrigerator (below 5°C) until further analysis. Sampling locations are shown in Fig.1.

Analytical Method
During analysis of aromatic NMHCs in the laboratory, charcoal from ORBO™-32 tubes were transferred into a 2-ml amber colour glass vial, 1 ml of CS₂ (99% purity) was added and put on the speed control spinix machine for agitation for 30 minute for the complete extraction of aromatic NMHCs from charcoal. The samples were extracted from amber colored glass vial through a syringe and put into other glass vials. These samples containing in glass vial were
preserved into the freezer at a temperature below 5°C. The prepared samples were analyzed using GC-FID equipped with a capillary column of 100% methyl silicone fused silica, as the dimension (60 mm × 0.25 mm, i.e.; film thickness, 1 mm; Supelco, eQuity-1) based on National Institute of Occupational Safety and Health method. 1ìL of prepared sample was taken through a micro syringe and injected into the gas chromatograph. The samples were run with initial oven temperature at 40°C for 5 min, hold time and then temperature raised at the rate of 10°C/ min up to 220°C, and kept for 4 min. Identification of NMHCs has done according to their retention time of calibrated standards (HC JMHW VOC Mix, 1000 ig/ml, in methanol) under a precise chromatographic conditions. Calibration standard mixture was diluted with acetone to different lower concentrations (0.0, 0.01, 0.1, 1.0, 10.0, 100.0 ppm).

For aliphatic NMHC analysis, we have taken 10-20 ml volume of concentrated sample at STP using gas tight syring ( purchased by Sigma Aldrich, India) and injected into the GC-FID system. High purity carrier gas(H2) with a flow rate of 25ml/min was used. Temperature of column program started from 35 °C for 1.2 min, and then raised at the rate of 12 °C/m, till it reached 65°C hold 1min. Again, the temperature was raised at the rate of 10 °C/min from 65 to 150 °C kept 2 min for the proper separation of compounds. The calibration gas mixture of 1ppm NMHCs of NIST calibration standard supplied by CHEMIX Speciality Gases, Bangalore, India, containing 17 component, used to calibrate Gas Chromatograph. Different concentration of calibration gas mixture(i.e.,0.0, 20, 50, 100, 200, 500 ppb) diluted using mass flow controller and analysed precisely in the same approach as for the air samples. The calibration standard mixture run every day to check the calibration curve. Detector response variation was less than 2% of the standard gas mixture. Data validity was confirmed through various steps. The result of the duplicate sample run was within 10 percent of the variation. Minimum detection limit of NMHCs compound was ranges from 0.10-0.30 ppb.

**PCA/APCS**

We have applied multivariate analysis, i.e., PCA/APCS to identification of source profile of NMHCs. For this tool, does not require prior information on source composition. The PCA used in air pollution is expressed in the equation(1):

\[
R_{ij} = \sum_{k=1}^{n} D_{ik} M_{kj}
\]

where, \( R_{ij} \) is the normalized value of the concentration level of the \( i \)th species for the \( j \)th sample. Total number of source is denoted by \( N \). \( M_{kj} \) is represents as a factor score of the \( k \)th common factor for the sample \( j \)th. Factor loadings of \( i \)th classes of the \( k \)th source is denoted as \( D_{ik} \) and it is estimated using eigen vector disintegration matrix\[34,40\]. The detailed study of factor analysis was done by Thurston and Spengler\[38\]. SPSS was used for data reduction factor analysis for possible source identification of NMHCs. APCS was used to assess the source distributions profile of each pollutant which was identified by PCA. PCA was performed by standardizing the variable data using the following equation(2):

\[
X_{ij} = \frac{Y_{ij} - \bar{Y}_j}{\sigma_j}
\]

where, \( Y_{ij} \) is the calculated concentration of variable \( j \)th in the sample \( i \)th, and \( \bar{Y}_j \) the sums average concentration of variable \( j \)th, while standard deviation is \( \sigma_j \). The normalized factor scores with zero mean is mentioned in equation (3):

\[
(B_0)_k = \sum_{j=1}^{J} P_{kj} (X_0)_j
\]

where, \( B_0 \) is normalized factor scores with unit standard deviation after PCA performed. \( B_0 \) is a factor scores at zero mean concentration each sample. While \( (P) \) represent as a factor scores coefficients obtained after PCA performance, and the value of \( (X_0)_j \) computed from equation (2). The total number of variables are represents by \( J \). APCS is estimated for each sample in each component by deducting the values of \( B_0 \) of each sample from the resulting values of \( B \) after PCA performance of the identical variables\[10,16\] shown in equation (4):

\[
APCS_k = (B_j)_ik \cdot (B_i)_k
\]

Multiple linear regression analysis was done for measured concentration of dependent variables by using mass of various sources as independent variables. The source contribution profile using multiple linear regression analysis\[10,41\] shown in the
following equation (5):

$$R_j = (q_0)_j + \sum_{k=1}^{r} q_{kj} \cdot APCS_k$$  \((5)\)

Where, \(R_j\) characterized to calculated concentration of sample \(j\). \((q_0)_j\) represent invariable term of multiple linear regression for pollutant \(j\) from unaccounted sources. The coefficient of multiple linear regression of the source \(k\) for pollutant \(j\) from accounted source is denoted by \(q_{kj}\). \(APCS_k\) term is representing the rotated absolute component score of the rotated factor \(k\) for the sample has been used in the above equation. The source profile is calculated from multiple linear regression between and \(q_{kj}\). These sources are further used to estimate the pollutant contribution from individual source.

**Results and Discussion**

**NMHCs Concentrations**

In the present study, we have summarized range, annual mean and standard deviation (SD) ambient concentration of selected NMHCs in the ambient air of metro city, Delhi (Table 1). The selected NMHCs compounds were found at all site with their similar composition. The presence of abundant concentration of aromatic hydrocarbons namely benzene, toluene, o-xylene and p/m-xylene indicates the vehicular as well as industrial emissions are common and dominant source of NMHCs compounds in the ambient air of Delhi. The sum of aliphatic hydrocarbon was found to be greater than that of the aromatic hydrocarbons. Fig.2 showed the mean concentration of isopentane was found to be highest followed cis-2-pentene>trans-2-butene>i-butane>n-pentane>1,3-butadiene>heptanes>propane of the aliphatic hydrocarbon and n-butane was observed to be lower. The mean concentration of isopentane indicates that it is emitted mostly from vehicular exhausts, secondary industrial process. On the other hand mean concentration of o-xylene estimated lower and toluene, benzene were highest among the aromatic hydrocarbon. These results reveal that the benzene was dominated at a traffic intersection, followed by industrial and other sites. It may be due to larger lifetime in ambient air and lesser reactivity.

An ambient mean concentration of benzene, toluene, xylene isomers and 1,3-butadine were observed

<table>
<thead>
<tr>
<th>Aliphatic Compound</th>
<th>LOD (ppb)</th>
<th>Range</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>0.3</td>
<td>BDL-158.8</td>
<td>41.25</td>
<td>36.34</td>
</tr>
<tr>
<td>n-butane</td>
<td>0.2</td>
<td>BDL-154</td>
<td>35.41</td>
<td>31.41</td>
</tr>
<tr>
<td>i-butane</td>
<td>0.1</td>
<td>3.61-277.5</td>
<td>49.99</td>
<td>44.5</td>
</tr>
<tr>
<td>trans-2-butene</td>
<td>0.1</td>
<td>2.54-259.2</td>
<td>56.59</td>
<td>55.03</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.2</td>
<td>BDL-197.64</td>
<td>46.29</td>
<td>38.25</td>
</tr>
<tr>
<td>i-pentane</td>
<td>0.2</td>
<td>3.02-363.4</td>
<td>90.65</td>
<td>76.71</td>
</tr>
<tr>
<td>trans-2-pentene</td>
<td>0.2</td>
<td>2.76-237.5</td>
<td>59.75</td>
<td>54.37</td>
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<tr>
<td>n-hexane</td>
<td>0.1</td>
<td>1.90-172.8</td>
<td>42.21</td>
<td>36.92</td>
</tr>
<tr>
<td>n-heptane</td>
<td>0.2</td>
<td>3.01-173.01</td>
<td>45.45</td>
<td>42.73</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Aromatic Compound</th>
<th>LOD (ppb)</th>
<th>Range</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.1</td>
<td>1.42-132.34</td>
<td>21.5</td>
<td>18.82</td>
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<tr>
<td>Benzene</td>
<td>0.2</td>
<td>.25-102.4</td>
<td>17</td>
<td>12.56</td>
</tr>
<tr>
<td>p/m-Xylene</td>
<td>0.3</td>
<td>BDL-61.4</td>
<td>12.07</td>
<td>11.44</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.2</td>
<td>BDL-53.1</td>
<td>10.87</td>
<td>11.93</td>
</tr>
</tbody>
</table>

LOD: Low detection limit, SD: Standard deviation, BDL: Below detection limit
to be similar and/or higher than that estimated in previous studies\textsuperscript{23,44–48}. It indicates that traffic area has heavy transportation load and their attributes are frequently inferred in urban air pollution. Apart of these, activities involved at polymer manufacturing industrial area, refinery operation and gas storage tank are the second and the third most alarming sites for urban air quality. At the same time, residential area and urban background area shows less contribution in the urban air pollution as compared to traffic and industrial site. The abundance of n-pentane and i-pentane in urban air is may be attributed diversity of fuel type used. The sources of n-hexane encountered in urban air is largely due to emission from polymer industry\textsuperscript{49}.

**Source Characteristics of NMHCs**

**Correlation Analysis**

Table 2 shows the correlation analysis, among the selected NMHCs compounds. The concentration of ambient NMHCs is used to the source identification and distribution pattern during sampling period. Karl’s Pearson correlation coefficient was found to be at 99 and 95 percent of significance level. In this study, the correlation coefficient value of \( r > 0.4 \), can be considered as a good correlation. Results showed the \( r \) value between the benzene and toluene was higher (0.651) among all NMHCs species. On the other hand \( r \) value between benzene and i-butane; n-pentane was found to be 0.346; 0.367 respectively. Similarly, \( r \) value between n-butane and o-xylene was found to be 0.449, and n-heptane and i-butene was found 0.412. These results are clearly shows that the \( r \) values among the selected compounds have approaches to high, good and lower, indicating the pollutants have more than one origin source, as an expected in the urban air of metro city Delhi. Benzene shows high positive correlation with toluene and lower with i-butane and n-pentane reveals that major source may be vehicle exhaust as well as other sources\textsuperscript{34,50}. In the present study, most of \( r \) value is \( d < 0.4 \), indicating that the sources of NMHCs pollutants have various origin. Overall, the \( r \) values among the NMHCs compounds are found to be \( r = 0.5 \pm 0.2 \), showed strong, moderate and low significance level. It is clearly indicates that the source NMHCs are may be vehicle exhaust, industrial, manufacturing industries, petrochemical, gas storage tank, secondary industrial process and many other sources\textsuperscript{24,34,50} while the percentage contribution of source emission is not reveal by this method.

**Characteristic Ratio of NMHCs**

After estimation of characteristic ratio,which may only reveal the source emissions of NMHCs in the ambient air metro city Delhi. Both aliphatic and aromatic NMHCs are key abundant compounds; some of these compounds (benzene, toluene, and xylene isomers) are important indicator of vehicular emissions source in the urban ambient air. The lifetime of benzene is higher due to its lower reactivity as compared to toluene in the urban sites\textsuperscript{15,30,43}. The higher ratio of xylene/benzene (X/B) indicates the fresh air masses and lower value indicates aged air masses\textsuperscript{51,52}. However, the higher ratio value describe the source have closer to the sampling site and their

![Fig. 2: Annual mean concentration of selected NMHCs](image-url)
Table 2: Correlation analysis among the selected NMHCs during sampling period at Delhi

<table>
<thead>
<tr>
<th></th>
<th>Propane</th>
<th>n-butane</th>
<th>i-butane</th>
<th>trans-2-butane</th>
<th>i-butene</th>
<th>1,3-butadiene</th>
<th>n-pentane</th>
<th>i-pentane</th>
<th>cis-2-pentene</th>
<th>n-hexane</th>
<th>n-heptane</th>
<th>Toluene</th>
<th>Benzene</th>
<th>p/m-xylene</th>
<th>o-xylene</th>
</tr>
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<tbody>
<tr>
<td>Propane</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-butane</td>
<td>0.067</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.327</td>
<td>0.127</td>
<td>0.101</td>
<td>0.157</td>
<td>0.574</td>
<td>0.216</td>
</tr>
<tr>
<td>i-butane</td>
<td>0.103</td>
<td>-0.225</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.064</td>
<td>-0.163</td>
<td>0.471**</td>
<td>0.223</td>
<td>0.341*</td>
<td>0.349**</td>
</tr>
<tr>
<td>trans-2-butane</td>
<td>0.226</td>
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<td>0.76</td>
<td>1</td>
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<td></td>
<td></td>
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<td></td>
<td>0.148</td>
<td>0.280</td>
<td>0.287</td>
<td>0.214</td>
<td>0.018</td>
<td>0.228</td>
</tr>
<tr>
<td>i-butene</td>
<td>0.300</td>
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<td></td>
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<td>-0.127</td>
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<td>0.197</td>
<td>0.024</td>
<td>0.192</td>
<td>0.176</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>0.244</td>
<td>0.148</td>
<td>0.280</td>
<td>0.287</td>
<td>0.214</td>
<td>1</td>
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<td></td>
<td>0.147</td>
<td>0.002</td>
<td>0.19</td>
<td>0.024</td>
<td>0.018</td>
<td>0.341*</td>
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<td></td>
<td>0.069</td>
<td>0.155</td>
<td>0.232</td>
<td>0.006</td>
<td>-0.131</td>
<td>0.341*</td>
</tr>
<tr>
<td>i-pentane</td>
<td>-0.064</td>
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<td>-0.127</td>
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<td>0.180</td>
<td>-0.116</td>
<td>-0.018</td>
<td>1</td>
<td></td>
<td>0.029</td>
<td>0.267</td>
<td>0.257</td>
<td>-0.045</td>
<td>0.016</td>
<td>0.651**</td>
</tr>
<tr>
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<td>0.367*</td>
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<td>0.192</td>
<td>-0.155</td>
<td>0.037</td>
<td>1</td>
<td>0.069</td>
<td>0.155</td>
<td>0.232</td>
<td>0.006</td>
<td>0.002</td>
<td>0.197</td>
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<td>0.166</td>
<td>0.134</td>
<td>0.028</td>
<td>0.412*</td>
<td>0.136</td>
<td>0.181</td>
<td>0.257</td>
<td>-0.045</td>
<td>-0.162</td>
<td>0.186</td>
<td>0.038</td>
<td>0.026</td>
<td>0.178</td>
<td>0.152</td>
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<tr>
<td>n-heptane</td>
<td>-0.101</td>
<td>0.094</td>
<td>0.056</td>
<td>0.186</td>
<td>0.018</td>
<td>0.341*</td>
<td>0.002</td>
<td>0.094</td>
<td>0.056</td>
<td>0.094</td>
<td>0.186</td>
<td>0.038</td>
<td>0.026</td>
<td>0.178</td>
<td>0.152</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.057</td>
<td>-0.184</td>
<td>0.346**</td>
<td>0.082</td>
<td>-0.162</td>
<td>0.367*</td>
<td>0.029</td>
<td>0.092</td>
<td>-0.016</td>
<td>0.082</td>
<td>0.184</td>
<td>0.346**</td>
<td>0.082</td>
<td>0.184</td>
<td>0.346**</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.574</td>
<td>0.216</td>
<td>0.449**</td>
<td>0.065</td>
<td>0.059</td>
<td>0.059</td>
<td>0.009</td>
<td>0.124</td>
<td>0.148</td>
<td>0.003</td>
<td>0.124</td>
<td>0.148</td>
<td>0.009</td>
<td>0.124</td>
<td>0.148</td>
</tr>
<tr>
<td>p/m-xylene</td>
<td>0.114</td>
<td>-0.059</td>
<td>-0.059</td>
<td>-0.166</td>
<td>-0.043</td>
<td>-0.237</td>
<td>-0.129</td>
<td>0.201</td>
<td>-0.045</td>
<td>0.056</td>
<td>0.031</td>
<td>0.116</td>
<td>0.045</td>
<td>0.116</td>
<td>0.275</td>
</tr>
<tr>
<td>o-xylene</td>
<td>-0.216</td>
<td>-0.449**</td>
<td>-0.065</td>
<td>-0.059</td>
<td>-0.009</td>
<td>-0.124</td>
<td>-0.148</td>
<td>0.003</td>
<td>-0.303</td>
<td>0.061</td>
<td>0.086</td>
<td>0.219</td>
<td>0.148</td>
<td>0.003</td>
<td>0.219</td>
</tr>
</tbody>
</table>

*95 percent of significance level (2-tailed).
**99 percent of significance level (2-tailed).
photochemical processes confer the lower impact on the concentration of NMHCs compound. On the other hand, most of the anthropogenic NMHCs are emitted from vehicular exhaust in the urban areas. Thus the ratio of benzene/toluene (B/T) can be used as a tracer source for the traffic site identification. The ratio of B/T generally is 
0.5, is considered for vehicular emission [35,35]. On the other hand B/T ratio is less than 0.5 indicate sources may be vehicles as well as other sources in the ambient air. In the present study, we found that the average mean concentration of toluene was higher than the benzene during the sampling period. Therefore, this B/T ratio is utilized to evaluate source emission in metro city Delhi. The ratio of B/T value was found to be 0.79 during the sampling period, which indicates vehicular sources, is the primary sources of NMHCs in urban air of Delhi [23,34]. The ratio of T/B is approaching to 1, indicates the traffic is dominated as a emission of sources and the value increases to greater than 1, then it indicates sources are close to the pollution source [35]. For the xylene isomers, the ratio value of B/o-X and B/mp-X were found to be e+1, indicated that the sources may be far from the sampling location during the winter and summer season. It may be influenced by the meteorological parameters and transportation of vehicles [49].

Principal Component Analysis (PCA)
Beside of correlation and characteristics ratio analysis, we have used well-established PCA to analyze in multivariate environmental data sets [16,41,56,57] for possible source profile identification (Table 3). Multivariate analyses of NMHCs is elucidate relationships between a set of correlated variables and identified a number of Principal Components (PC), it may explain the variance of data set [58]. The estimated NMHCs data are arranged with low or high concentrations for the possible outlier, before applying the PCA model. The varimax rotated factor analysis was applied on an estimated data of NMHCs and found the possible source profile of NMHCs in the urban air in Delhi. In general, eigenvalues larger than 1.0 are chosen for factors or principle components (PCs) [34,59]. Higher factor loading of marker compound is considered to identify the possible source profile of NMHCs [40]. In the present study, six PCs were extracted after varimax rotation for the identification of possible sources profile of NHMCs. For identification of possible source profile associated with origin, factor loading of marker compound is to be considered greater than 0.4. The total cumulative % of variance elucidated by six factors or PC and accounted about 70.0 % of dataset. The first factor was explaining 16.2% of the total variance of a data set with high loadings of benzene, toluene, p/m-xylene and o-xylene which may emitted from combustion process. Thus, the first factor is attributed to the vehicular exhausts as a possible sources profile [34,49,58]. In the metro city, Delhi, as per traffic police Delhi websites has mentioned about 96 lakh vehicles in Delhi, most of them are private and operated daily (https://delhitrafficpolice.nic.in/). They have various fuel types consumption like petrol (gasoline), liquefied petroleum gas, compressed natural gas (CNG) and diesel. Most of the heavy vehicles (truck, buses) and fewer light vehicles (taxis) are using diesel as a fuel. While most of the car, auto rickshaw are using both petrol and CNG as a fuel. These fuels are emitted large amount of both aliphatic and aromatics hydrocarbons and leads to elevate the level of NMHCs into the ambient air of metro city Delhi. Aromatic NMHCs benzene, toluene and p/m-xylene are mostly emitted from vehicular exhausts [34,50]. These are the byproduct of fuel combustion, but unburned gasoline is not produced much concentration of the toluene, and p/m-xylene [35]. The second factor is explaining about 14.86% of the percentage variance of a data set with high loadings of iso-2-pentene, n-hexane and 1,3-butadiene and indicates polymer manufacturing industries are the major source profile [34]. A third factor is to be identified as a refinery operation/gas station/storage tank/internal combustion of vehicles which explained about 11.86% of data set, associated with high loadings of n-pentane, iso-butane, n-heptane, trans-2-butane and 1,3-butadiene [34,49,60,61]. NMHCs including iso-butane associated with fourth factor which is explaining about 11.11% of data set. They are characterized as flaring emission as a source profile. Fifth factor is classified as a natural gas emission which is accounted about 8.54% of data set with high loadings of isobutene. However, the sixth profile characterized by a secondary industrial process, including paints, body soaps, metal fabricators and processing as major contributors which explained about 7.36% of dataset with high loadings of iso-pentane, and trans-2-butene [34,49,58].
In the present study, we have calculated APCS based on the PC scores and true zero PC and these values are applied for quantification of various source profile. Further on the basis of observed APCS, we have executed the multiple linear regression analysis of the measured concentration of each compound. The coefficient of the equation is calculated by using concentration of each NMHCs compound participated in the source identification. Fig. 3 showed vehicular emission source profile was estimated about (23%) of total mass apportionment in the urban ambient air of Delhi. Polymer manufacturing industries emitted approximately 19% of total mass apportionment in the urban urban air, indicates polymer industry was the emission source profile. The ratio of B/T value also confirmed that the vehicular source profile, was the main sources of NMHCs in urban air of Delhi. In the present study, the PCA/APCS receptor model is applied for the percentage contribution of possible source profile of NMHCs. Six factors after varimax rotation and explained about 70.0% of data set of NMHCs. Further multiple linear regression analysis based on APCS of the measured concentration of each compound. As a result the vehicular emission source was found to be dominant source and accounted about (23%) of total mass apportionment in the urban ambient air. Whereas polymer manufacturing

### Table 3: Factor loadings matrix after varimax rotation of PCA analysis

<table>
<thead>
<tr>
<th>Compound</th>
<th>PC1</th>
<th>PC2</th>
<th>PC3</th>
<th>PC4</th>
<th>PC5</th>
<th>PC6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>-.176</td>
<td>.177</td>
<td>.071</td>
<td>-.028</td>
<td>-.677</td>
<td>-.067</td>
</tr>
<tr>
<td>n-butane</td>
<td>-.138</td>
<td>.157</td>
<td>-.167</td>
<td>.317</td>
<td>.779</td>
<td>.009</td>
</tr>
<tr>
<td>iso-butane</td>
<td>.200</td>
<td>.101</td>
<td>.754</td>
<td>.144</td>
<td>-.126</td>
<td>-.199</td>
</tr>
<tr>
<td>trans-2-butane</td>
<td>-.202</td>
<td>.380</td>
<td>.485</td>
<td>-.356</td>
<td>.124</td>
<td>.426</td>
</tr>
<tr>
<td>iso-butene</td>
<td>.061</td>
<td>.025</td>
<td>-.026</td>
<td>.870</td>
<td>.063</td>
<td>-.010</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>-.467</td>
<td>.403</td>
<td>.432</td>
<td>.311</td>
<td>.104</td>
<td>-.194</td>
</tr>
<tr>
<td>n-pentane</td>
<td>.175</td>
<td>-.120</td>
<td>.792</td>
<td>-.011</td>
<td>-.104</td>
<td>.074</td>
</tr>
<tr>
<td>iso-pentane</td>
<td>.017</td>
<td>-.070</td>
<td>.135</td>
<td>.200</td>
<td>-.110</td>
<td>.850</td>
</tr>
<tr>
<td>cis-2-pentene</td>
<td>.117</td>
<td>.761</td>
<td>-.149</td>
<td>.068</td>
<td>.186</td>
<td>.132</td>
</tr>
<tr>
<td>n-hexane</td>
<td>.141</td>
<td>.738</td>
<td>.067</td>
<td>.049</td>
<td>-.165</td>
<td>-.092</td>
</tr>
<tr>
<td>n-heptane</td>
<td>.022</td>
<td>-.081</td>
<td>.680</td>
<td>.182</td>
<td>.029</td>
<td>.328</td>
</tr>
<tr>
<td>Toluene</td>
<td>.770</td>
<td>.073</td>
<td>.282</td>
<td>.160</td>
<td>.073</td>
<td>.161</td>
</tr>
<tr>
<td>Benzene</td>
<td>.846</td>
<td>.009</td>
<td>.274</td>
<td>.058</td>
<td>.063</td>
<td>.079</td>
</tr>
<tr>
<td>p/m-xylene</td>
<td>.528</td>
<td>.005</td>
<td>-.299</td>
<td>-.101</td>
<td>.085</td>
<td>.348</td>
</tr>
<tr>
<td>o-xylene</td>
<td>.653</td>
<td>-.254</td>
<td>-.037</td>
<td>-.149</td>
<td>.238</td>
<td>-.132</td>
</tr>
<tr>
<td>Eigen value</td>
<td>2.44</td>
<td>2.23</td>
<td>1.78</td>
<td>1.67</td>
<td>1.28</td>
<td>1.10</td>
</tr>
<tr>
<td>% variance</td>
<td>16.2714</td>
<td>86.11</td>
<td>87.11</td>
<td>8.54</td>
<td>7.36</td>
<td></td>
</tr>
<tr>
<td>% CV</td>
<td>16.2731</td>
<td>13.43</td>
<td>0.054</td>
<td>12.62</td>
<td>6.670.02</td>
<td></td>
</tr>
</tbody>
</table>

CV: Cumulative Variance; PC: Principle component; Factor loadings values were chosen greater than 0.4 for the possible source identification.

### Absolute Principal Component Scores (APCS)

In the present study, we have calculated APCS based on the PC scores and true zero PC and these values are applied for quantification of various source profile. Further on the basis of observed APCS, we have executed the multiple linear regression analysis of the measured concentration of each compound. The coefficient of the equation is calculated by using concentration of each NMHCs compound participated in the source identification. Fig. 3 showed vehicular emission source profile was estimated about (23%) of total mass apportionment in the urban ambient air of Delhi. Polymer manufacturing industries emitted approximately 19% of total mass apportionment in the urban urban air, indicates polymer industry was the emission source profile. The ratio of B/T value also confirmed that the vehicular source profile, was the main sources of NMHCs in urban air of Delhi. In the present study, the PCA/APCS receptor model is applied for the percentage contribution of possible source profil of NMHCs. Six factors after varimax rotation and explained about 70.0% of data set of NMHCs. Further multiple linear regression analysis based on APCS of the measured concentration of each compound. As a result the vehicular emission source was found to be dominant source and accounted about (23%) of total mass apportionment in the urban ambient air. Whereas polymer manufacturing industries emitted approximately 19% of total mass apportionment in the urban ambient air, indicates polymer industry was the emission source profile. The ratio of B/T value also confirmed that the vehicular source profile, was the main sources of NMHCs in urban air of Delhi. In the present study, the PCA/APCS receptor model is applied for the percentage contribution of possible source profil of NMHCs. Six factors after varimax rotation and explained about 70.0% of data set of NMHCs. Further multiple linear regression analysis based on APCS of the measured concentration of each compound. As a result the vehicular emission source was found to be dominant source and accounted about (23%) of total mass apportionment in the urban ambient air. Whereas polymer manufacturing industries emitted approximately 19% of total mass apportionment in the urban ambient air, indicates polymer industry was the emission source profile. The ratio of B/T value also confirmed that the vehicular source profile, was the main sources of NMHCs in urban air of Delhi. In the present study, the PCA/APCS receptor model is applied for the percentage contribution of possible source profil of NMHCs. Six factors after varimax rotation and explained about 70.0% of data set of NMHCs. Further multiple linear regression analysis based on APCS of the measured concentration of each compound. As a result the vehicular emission source was found to be dominant source and accounted about (23%) of total mass apportionment in the urban ambient air. Whereas polymer manufacturing

### Source emissions of NMHCs

![Source emissions of NMHCs](source_emissions.png)

**Conclusion**

An ambient concentration of the fifteen different NMHCs were calculated in the metro city Delhi during the winter and summer season. An abundant concentration of benzene, toluene, o-xylene, p/m-xylene indicates it is emitted primarily from vehicular emissions. The average concentration of iso-pentane and cis-2-pentene were found to be highest among the selected NMHCs. It may emitted from vehicular exhausts (fuel types used) as well as secondary industrial processes. The presence of n-hexane in urban air, indicates polymer industry was the emission source profile. The ratio of B/T value also confirmed that the vehicular source profile, was the main sources of NMHCs in urban air of Delhi. In the present study, the PCA/APCS receptor model is applied for the percentage contribution of possible source profil of NMHCs. Six factors after varimax rotation and explained about 70.0% of data set of NMHCs. Further multiple linear regression analysis based on APCS of the measured concentration of each compound. As a result the vehicular emission source was found to be dominant source and accounted about (23%) of total mass apportionment in the urban ambient air. Whereas polymer manufacturing..
industries (19%), refinery operation/gas station/storage tank (14%), flare emissions (13%), natural gas emissions (10%), secondary industrial process, including paints, body soaps, and metal fabricator and processing (8%) and remaining 13% was found to be an unidentified source. Over all results of this study showed the level of NMHCs has been increased and lead to worsen air quality in the metropolis, Delhi. Therefore, the most effective way to avoid health hazard to the urban communities caused via air pollution required preventive measure for the mitigation of major source profile of NMHCs.

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