Monthly and Seasonal Variations in Aerosol Associated \(n\)-alkane Profiles in Relation to Meteorological Parameters in New Delhi, India

Shweta Yadav, Ankit Tandon, Arun K. Attri*  
School of Environmental Sciences, Jawaharlal Nehru University, New Delhi – 110067, India

ABSTRACT

A one-year extensive investigation to assess monthly and seasonal variations in the PM\(_{10}\) associated homologous series of \(n\)-alkane (C\(_{11}\)–C\(_{35}\)) profiles was carried out in New Delhi, India. Quantitative estimation of \(n\)-alkanes, involving 3–4 PM\(_{10}\) samples/month, was done by using thermal desorption gas chromatography mass spectrometry (TD-GC-MS). Significant seasonal variations were observed, both in mass concentrations (annual mean: 517 ± 256 ng/m\(^3\)) and mass fractions (annual mean: 4368 ± 2067 ppm) of total \(n\)-alkanes (C\(_{11}\)–C\(_{35}\)). The impact of the Planetary Boundary Layer (PBL) on the \(n\)-alkane profiles was the most significant among all the meteorological parameters considered. A strong positive correlation (\(r = 0.84\)) between PM\(_{10}\) load (\(\mu\)g/m\(^3\)) and mass concentrations of total \(n\)-alkanes (ng/m\(^3\)) was observed; whereas a negative correlation (\(r = –0.72\)) was seen between the PM\(_{10}\) load and mass fractions of total \(n\)-alkanes (ppm). Annual mean values of the Carbon Preference Index (CPI) and Wax \(n\)-alkanes percentage (WNA%) stood at 2.2 ± 0.6 and 39 ± 10%, respectively. Established diagnostic tools indicated that during autumn, the dominant inputs of aerosol associated \(n\)-alkanes came from petrogenic (vehicular and industrial) emissions (72 ± 7%), with lesser contributions from biogenic activities (28 ± 7%). In other seasons, although petrogenic sources remained a dominant contributor (53 ± 6%–59 ± 14%), the contributions from biological sources were also comparable (41 ± 14%–47 ± 6%). Emissions of total \(n\)-alkanes from both petrogenic and biogenic sources were maximum during spring. In the rest of the months, small variations were observed in the emissions of total \(n\)-alkanes from petrogenic sources, whereas large variations were noted in the emissions from biogenic sources.

Keywords: Aerosols; \(n\)-alkanes; TD-GC-MS; Seasonal variations; Diagnostic parameters.

INTRODUCTION

Presence of aerosols in ambient atmosphere is a manifestation of natural and anthropogenic source(s) and process(es). Their concentration, size-distribution and chemical composition varies in time and bear location specific fingerprints (Seinfeld and Pandis, 1998; Pitts and Pitts, 1999). These variations are linked to the nature and strength of the emitting source(s), location specific geochemical and meteorological characteristics (Yadav and Rajamani, 2004; Tandon et al., 2010).

Compositionally, carbonaceous constituents comprise a significant fraction of aerosol load and are generally composed of black carbon or elemental carbon (BC or EC) and a complex mixture of large variety of organic species designated as Organic Carbon (OC); OC is an important part of atmospheric aerosols that constitute ~10–70% of the total dry fine particle mass (Turpin et al., 2000) and is ubiquitous throughout the troposphere (Hildemann et al., 1996; Jacobson et al., 2000). OC fraction represents transient carbon pool in the atmosphere, it is known to significantly affect the radiative forcing (Dickerson et al., 1997; Jacobson et al., 2000), cloud formation (Novakov and Corrigan, 1996; Sun and Ariya, 2006; Andreae and Rosenfeld, 2008) and human health (Pope, 2000; Pope et al., 2004). Thus, chemical characterization and quantitative estimation of OC associated with ambient aerosols in relation to their variability in time and space has emerged as an important area of research in recent years (Penner and Novakov, 1996; Gelencsér, 2004; Sachdeva and Attri, 2008).

It is reasonably well established that aerosol associated OC fraction represents a complex diverse mixture of; predominantly, aliphatic and aromatic hydrocarbons [\(n\)-alkanes, alkenes, Polycyclic Aromatic Hydrocarbons (PAHs)], \(n\)-alkanals, \(n\)-alkanols, \(n\)-alkanoic acids and to a lesser extent dicarboxylic acids, carbonyl and carboxylic compounds etc. (Stephanou, 1992; Abas and Simoneit, 1996; Simoneit, 1999; Jacobson et al., 2000; Miyazaki et al., 2009; Fu et al., 2010). With reference to aerosol associated OC fraction, homologous series of \(n\)-alkanes is most frequently investigated; \(n\)-alkanes are known to be stable, non-polar as well as reasonably refractory aliphatic hydrocarbons and are relatively straightforward to gas chromatography
analysis. Characterization of aerosol associated \( n \)-alkanes, on the basis of the related diagnostic parameters reflect on their origin from, (a) biogenic sources- leaf abrasion products, garden soil, biomass burning etc., and (b) anthropogenic sources- tire debris, organometallc brake lining dust, cigarette smoke, vehicular and industrial emissions etc. (Simoneit, 1999; Rogge et al., 1991, 1993a, b, c; Kadowaki, 1994; Rogge et al., 1994; Rogge et al., 1997, 1998; Schauer et al., 1999, 2001; Mandalakis et al., 2002; Schauer et al., 2002; Young and Wang, 2002; Andreou et al., 2008; Kotianová et al., 2008).

Presence of year round high aerosol load in the ambient urban environment, in India, is a common feature, which is related to high population density and rising industrial and vehicular emissions (Mitra and Sharma, 2002); under these conditions, only few scientific investigations have been done to comprehend the distribution profile of particle bound \( n \)-alkanes in relation to the sources of aerosol associated OC (Sharma et al., 2003; Chowdhury et al., 2007; Fu et al., 2010). Sharma et al. (2003) collected ten eight-hourly samples of PM\(_{10}\) aerosols, at a residential location in New Delhi from December 2001 to March 2002. For source identification, they used \( n \)-Alkanes (C\(_{21}\)–C\(_{31}\)), PAHs and other marker compounds and concluded vehicular emissions and biomass and/or refuse burning as the significant contributors. Another investigation done in four urban settings (Delhi, Mumbai, Kolkata, and Chandigarh) by Chowdhury et al. (2007), estimated particle-phase organic compounds in PM\(_{2.5}\) aerosols over four seasons, on the basis of the analysis of one-two samples collected at a receptor site/season; these estimates were used for source apportionment using Chemical Mass Balance approach. It was reported that, on an average, primary emissions from fossil fuel combustion (coal, diesel, and gasoline) accounts for 25–33% and from biomass combustion about 7–20% of PM\(_{10}\) mass in Delhi. While investigating organic molecular composition of PM\(_{10}\) samples, collected in winter and summer season at Chennai, Fu et al. (2010) recognized fossil fuel combustion (24–43%) as the most significant source for the total identified compounds, followed by plastic emission (16–33%), secondary oxidation (8.6–23%), microbial/marine sources (7.2–17%), terrestrial plant waxes (5.9–11%) and biomass burning (4.2–6.4%). In an another comprehensive study done on organic aerosols in New Delhi, for the first time Miyazaki et al. (2009), characterised water-soluble dicarboxylic acids and bulk water soluble OC (WSOC). The average ratio between total WSOC and OC was found to be significantly higher during day (37%) than in the night (25%). When compared to other urban sites in Asia, they noticed higher average concentrations of oxalic acid (1.43 \( \mu \)g/m\(^3\)) and total diacids (2.33 \( \mu \)g/m\(^3\)). Importantly, less water-soluble OC and potassium were found to be highly correlated in both daytime and night-time samples, indicating the effect of emissions from biomass burning. Present status from these reported investigations, particularly from Delhi-specific locations, does provide tentative understanding about the profiling and diversity of OC associated with PM\(_{10}\) and PM\(_{2.5}\) aerosol size fractions without taking into consideration the associated diagnostic parameters; moreover, explanation put forth on their seasonal variability was constrained by the paucity of the number of samples representing a season. Interpretation was devoid of any considerations arising on account of the expected variations in meteorological variables: it is established that these variables affect significantly the changes encountered in the composition variability of aerosols (Seinfeld and Pandis, 1998; Pitts and Pitts, 1999).

Taking into account the present status of OC associated aerosol source profiling—in urban region of Delhi inflicted with year round high aerosol load—we extend the existing understanding by undertaking a comprehensive year round investigation, where 3–4 samples/month were collected and analyzed over 12 months at a known receptor site (Singh et al., 1997); samples were analyzed for the presence of homologous series of \( n \)-alkanes (C\(_{11}\)–C\(_{33}\)) using Thermal Desorption Gas Chromatography Mass Spectrometry (TD-GC/MS). Monthly distribution profile of \( n \)-alkanes in association with established diagnostic parameters (a) carbon preference index (CPI), (b) carbon number with maximum concentration (C\(_{\text{max}}\)), (c) wax \( n \)-alkanes from plants (WNA%), and (d) mass-weighted averaged chain length (ACL) were used to assess the variability in the source(s) of \( n \)-alkanes associated with aerosols. Role of meteorological parameters on monthly and seasonal variability in the distribution profile of \( n \)-alkanes, from the estimated associated diagnostic parameters was assessed in relation to PM\(_{10}\) samples.

**METHODS**

\( n \)-Alkanes associated with PM\(_{10}\) aerosol samples were analyzed by using gas chromatography-mass spectrometry (GC-MS), equipped with thermal desorption (TD) unit. The method was suitably developed to detect thermally desorbed organic compounds, directly, from aerosols collected on to filter matrix; this approach minimized the steps and errors involved as pose to the chemical extraction methods (Falkovich and Rudich, 2001; Hays and Lavrich, 2007; Shesley et al., 2007), requires less processing time, and little sample amount. Identification and quantification of \( n \)-alkane homologues was done with reference to \( n \)-alkane standards (C\(_{10}\) to C\(_{30}\) homologues obtained from Dr. Ehrenstorfer GmbH and Sigma–Aldrich), using TD-GC-MS method (Waterman et al., 2000; Ho et al., 2011).

**Sampling Details**

a) **Description of Sampling Site**

The capital region of Delhi is geographically located between 28°25′N and 28°53′N; 76°50′E and 77°22′E at 216 m above MSL in the northern part of India. It has a semi-arid climate influenced by the Himalayan ranges to the north, Thar desert to the west, the central hot plains to the south and hilly region to the northeast. Having population of about 1,67,53,235 inhabitants (Census, 2011), NCT region of Delhi has the dubious distinction of being one of the most polluted cities in the world and is afflicted with unusually high concentration of aerosol load in the lower
atmosphere (Yadav and Rajamani, 2006; Tandon et al., 2008, 2010). Large amounts of wind-blown dust during summers and a regular feature of ground-based temperature inversion with low planetary boundary layer (PBL) conditions, during winter season further amplifies the load in the city. The location selected for this experiment, Jawaharlal Nehru University (JNU), is a known receptor site (Singh et al., 1997) and has comparatively low vehicular traffic. The site is located in south Delhi ridge area, which forms a plateau of 250–300 m elevation above mean sea level and is approximately 100 m above the surrounding area. Sequential samples of PM$_{10}$ were collected on the rooftop of a building at 15 m height.

**b) Sample Collection**

PM$_{10}$ (aerodynamic diameter < 10 μm) aerosol samples were collected on pre-baked quartz-microfibre filter matrix using a respirable dust sampler (Envirotech, model–APM 460 BL). Samples were collected every fourth day of a week, for 24 hours duration, over a span of one year time period starting from 4th January 2007 to 28th December 2007.

All filter papers were prebaked at 450°C and stored under controlled temperature and relative humidity conditions, prior to their weighing. After sampling filters were stored in clean A4 size butter paper envelopes. These bags were further covered with aluminum foil to inhibit their exposure to light and were refrigerated until analysis. Samples were weighed before and after sampling on a well calibrated microbalance with a precision of 0.1 mg.

**Analysis of Aerosol Samples on TD-GC-MS**

A uniform disc of 25 mm diameter was stamped out by using fabricated stamping tool (stainless steel) from the filter with deposited aerosol sample; longitudinally cut sections of this disc were inserted into the TD tubes (SS PE ATD Tube 25049; Supelco, Bellefonte, PA, USA). Each sample was surrounded with pre-baked, Silane purged with high purity N$_2$ gas. All samples were prepared in clean A4 size butter paper envelopes. These bags were further covered with aluminum foil to inhibit their exposure to light and were refrigerated until analysis. Samples were weighed before and after sampling on a well calibrated microbalance with a precision of 0.1 mg.

Identification and Quantitative Estimation of n-Alkanes

Identification of desorbed n-alkanes was based on the presence of (1) molecular ion peak, (2) distinctive peak cluster fragmentation pattern, and (3) the largest peak (C$_{n}$H$_{2n+1}$) present in the cluster at m/z = 14n + 1. Characteristic m/z lines searched for n-alkanes were at 43, 57, 71, 85, 99 with the base peak at m/z 57 and sometimes occurring at m/z 43, representing the stable butyl (C$_{4}$H$_{9}$)$^+$ and propyl (C$_{3}$H$_{7}$)$^+$ ions respectively (Silverstein and Webster, 2008). Symmetrical narrow peaks of individual n-alkanes were identified in samples by comparison of their chromatographic retention times and fragmentation pattern present in standard runs with the assistance of inbuilt NIST and Wiley mass spectral libraries.

Quantitative estimation of desorbed n-alkanes associated with aerosols was done by using two standard mix: (1) n-alkanes standard mixture (Alkanes Mix 10, consisted of C$_{10}$ to C$_{15}$ homologues obtained from Dr. Ehrenstorfer GmbH, Augsburg, Germany), and (2) n-alkanes C$_{21}$ to C$_{30}$ standard solution 04071, Sigma–Aldrich (Bornem, Belgium), following the protocol optimized for the aerosol samples. Five different volumes of the standard mix, representing increasing concentrations, were spotted on blank filter discs (25 mm diameter, EPM 2000), and loaded into TD tubes by following the same procedure as explained earlier. In all, seven independent sets of standards were run, the mean peak area from these runs for respective resolved n-alkane were used to create a standard curve for each alkane.
present in the standard mix as a function of concentration; mean standard curves were used to quantify the $n$-alkanes present in the aerosol samples. Calibration was not found to be linear above $C_{35}$ $n$-alkane.

**Diagnostic Parameters and Source Apportionment**

Four established methods were used to assess the contributing source types: Carbon Preference Index (CPI), carbon number of the most abundant $n$-alkanes (Cmax), the contribution of wax $n$-alkanes from plants (WNA%), and higher plant $n$-alkane average chain length (ACL). CPI is a measure of odd to even carbon number predominance, and identifies contributions arising from biogenic and anthropogenic inputs (Bray and Evans, 1961; Abas and Simoneit, 1996; Kavouras et al., 1999; Pio et al., 2001; Alves et al., 2009) CPI, spanning for $C_{11}$–$C_{35}$ alkanes, is calculated by using following relation,

$$\text{CPI} = \frac{\sum_{i=13}^{35} C_i}{\sum_{k=12}^{34} C_k}$$  \hspace{1cm} (1)

where, $i$ takes odd and $k$ even carbon number $n$-alkane values in above relation (Simoneit, 1989; Alves, 2008).

WNA is calculated by subtraction of the average of next higher and previous lower even numbered carbon $n$-alkane homologues present in the sample, negative values are taken as zero; following expression is used for the calculations of WNA and its percentage:

$$\text{WNA}_{C_n} = \left[C_n \right] - \left(\frac{C_{n+1} + C_{n-1}}{2}\right)$$  \hspace{1cm} (2)

$$\text{WNA}\% = \frac{\sum_{n} \text{WNA}_{C_n}}{\sum_{n} \text{NA}} \times 100$$  \hspace{1cm} (3)

WNA\% gives the percentage concentration input of wax $n$-alkanes in sample, where $\Sigma \text{WNA}_{C_n}$ is the concentration sum of wax $n$-alkane contribution arising from all odd $n$-alkanes and $\Sigma \text{NA}$ is the concentration sum of total $n$-alkanes. Odd $n$-alkanes, especially of higher molecular weight are representatives of plant wax related emissions and are thus used to assess the biogenic contributions of $n$-alkanes in percentage. These epicuticular plant waxes are present on the surface of plant parts especially leaves in the form of multi-structural crystalline protrusions and are known to become airborne by various direct and indirect mechanisms like wind action or biomass burning (Simoneit et al., 1991a, b; Alves, 2008).

As aerosol associated $n$-alkanes can originate either from plant waxes or from petroleum combustion, percentage of petrogenic $n$-alkanes (PNA\%) can easily be calculated as:

$$\text{PNA}\% = 100 - \text{WNA}\%$$  \hspace{1cm} (4)

Cmax corresponds to the most abundant $n$-alkane of the homologous series, and is considered to be the strongest indicator for biogenic inputs. Cmax, at $C_{23}$ and $C_{25}$ serves as a marker for diesel exhaust, whereas $C_{max} \geq C_{23}$ indicates inputs arising from higher plant waxes (Simoneit, 1989).

ACL index, a proxy for temperature and humidity related emissions of $n$-alkanes from plants represents the average number of carbon atoms per molecule, based on the abundance of odd carbon numbered higher plant $n$-alkanes (Poynter and Eglington, 1990; Jeng, 2006; Alves, 2008), and is expressed as:

$$\text{ACL (n-alkanes)} = \frac{23 \times (C_{23}) + 25 \times (C_{25}) + \ldots + 33 \times (C_{33}) + 35 \times (C_{35})}{(C_{23}) + (C_{25}) + \ldots + (C_{33}) + (C_{35})}$$  \hspace{1cm} (5)

**Meteorological Variables**

Three hourly values of meteorological variables; planetary boundary layer (PBL), ambient temperature (T), dew point (Dp), relative humidity (RH) and wind speed (WS), corresponding with the duration of aerosol sample collection time span, were procured from Air Resources Laboratory, National Oceanic and Atmospheric Administration (http://www.arl.noaa.gov/READYamet.php) for the region of this study. As minimum of 3–4, 24 hourly PM10 samples were collected in each month, to reflect the corresponding variation in meteorological parameter, we use their respective mean values. Respective month’s values were pooled to represent that month’s mean value with standard deviation for PBL, T, RH and WS (Table 1).

**RESULTS AND DISCUSSION**

**PM10 Load and Mass Concentration of Total n-alkanes**

In Table 1, monthly average PM10 loads ($\mu$g/m$^3$) along with the monthly average values of meteorological variables are tabulated. Overall, there exists a significant positive correlation ($R^2 = 0.63$) between Dp and $n$-alkanes fraction (ppm). In contrast, there exists a significant negative correlation between Dp and $n$-alkanes concentration (ng/m$^3$) ($R^2 = -0.51$), as well as between Dp and PM10 load ($\mu$g/m$^3$) ($R^2 = -0.72$). It is observed that in the months of June–September, when region receives monsoonal rainfall, both Dp and $n$-alkanes fraction (ppm) have the highest values. Here, possible explanation might be traced into the hydrophobic properties of $n$-alkanes that could result into lesser wet deposition of $n$-alkanes as compared to other constituents of crustal origin. RH is also exhibiting almost similar relationship but with weaker correlations, however WS showed negligible correlations.

Large variation in PM10 load is noticeable with a minimum $40 \pm 6$ $\mu$g/m$^3$ in July to maximum $287 \pm 18$ $\mu$g/m$^3$ in April. Mean annual PM10 load, over 12 months span, was $151 \pm 94$ $\mu$g/m$^3$ which is much higher than National and International Standards (CPCB, USEPA). In broad agreement with diagnostic parameters (Table 2), total $n$-alkanes ($C_{11}$–$C_{35}$) also showed strong seasonal variation. The mean annual
Table 1. Monthly average values of PM_{10} load (µg/m^3), total n-alkane concentration (ng/m^3), scaled total n-alkane concentration (ng/m^3), mass fractions of total n-alkanes (ppm) and meteorological parameters.

<table>
<thead>
<tr>
<th>Month</th>
<th>PM_{10} (µg/m^3)</th>
<th>PBL (meter)</th>
<th>T (°C)</th>
<th>Dp (°C)</th>
<th>RH (%)</th>
<th>WS (Knots)</th>
<th>Σn-Alk (ng/m^3)</th>
<th>DCF</th>
<th>Σn-Alk (ng/m^3) Scaled*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan</td>
<td>226 ± 101</td>
<td>309.4 ± 53.9</td>
<td>10.9 ± 0.6</td>
<td>1.4 ± 1.5</td>
<td>54.2 ± 4.6</td>
<td>6.1 ± 1.6</td>
<td>790 ± 370</td>
<td>0.46 ± 0.08</td>
<td>354 ± 135</td>
</tr>
<tr>
<td>Feb</td>
<td>123 ± 65</td>
<td>401.1 ± 38.2</td>
<td>15.7 ± 0.6</td>
<td>7.8 ± 3.0</td>
<td>62.2 ± 10.8</td>
<td>5.1 ± 2.7</td>
<td>442 ± 142</td>
<td>0.60 ± 0.06</td>
<td>269 ± 113</td>
</tr>
<tr>
<td>Mar</td>
<td>98 ± 36</td>
<td>565.7 ± 73.7</td>
<td>19.8 ± 5.3</td>
<td>6.9 ± 1.7</td>
<td>46.8 ± 12.0</td>
<td>4.8 ± 1.8</td>
<td>179 ± 142</td>
<td>0.84 ± 0.11</td>
<td>153 ± 125</td>
</tr>
<tr>
<td>Apr</td>
<td>287 ± 18</td>
<td>1495.9 ± 525.9</td>
<td>31.9 ± 12.2</td>
<td>4.8 ± 7.3</td>
<td>21.0 ± 11.2</td>
<td>4.3 ± 0.8</td>
<td>824 ± 289</td>
<td>2.23 ± 0.78</td>
<td>1947 ± 1288</td>
</tr>
<tr>
<td>May</td>
<td>120 ± 24</td>
<td>1393.8 ± 287.0</td>
<td>34.4 ± 1.0</td>
<td>9.9 ± 3.3</td>
<td>24.6 ± 7.1</td>
<td>3.6 ± 1.3</td>
<td>529 ± 131</td>
<td>2.07 ± 0.43</td>
<td>1125 ± 497</td>
</tr>
<tr>
<td>Jun</td>
<td>61 ± 2</td>
<td>1095.7 ± 126.9</td>
<td>33.1 ± 12.2</td>
<td>20.3 ± 0.0</td>
<td>48.2 ± 3.5</td>
<td>5.3 ± 2.3</td>
<td>392 ± 22</td>
<td>1.63 ± 0.19</td>
<td>638 ± 38</td>
</tr>
<tr>
<td>Jul</td>
<td>40 ± 6</td>
<td>786.4 ± 157.5</td>
<td>32.2 ± 1.9</td>
<td>23.3 ± 2.0</td>
<td>61.8 ± 13.6</td>
<td>3.6 ± 0.9</td>
<td>333 ± 56</td>
<td>1.17 ± 0.23</td>
<td>389 ± 94</td>
</tr>
<tr>
<td>Aug</td>
<td>57 ± 13</td>
<td>718.1 ± 123.7</td>
<td>30.3 ± 0.9</td>
<td>22.7 ± 1.6</td>
<td>65.6 ± 9.6</td>
<td>4.3 ± 0.9</td>
<td>408 ± 73</td>
<td>1.07 ± 0.18</td>
<td>445 ± 160</td>
</tr>
<tr>
<td>Sep</td>
<td>59 ± 29</td>
<td>546.0 ± 142.7</td>
<td>28.0 ± 2.4</td>
<td>22.4 ± 2.7</td>
<td>74.4 ± 14.6</td>
<td>3.0 ± 0.4</td>
<td>256 ± 74</td>
<td>0.81 ± 0.21</td>
<td>207 ± 76</td>
</tr>
<tr>
<td>Oct</td>
<td>198 ± 50</td>
<td>591.4 ± 178.5</td>
<td>23.9 ± 0.7</td>
<td>7.4 ± 4.4</td>
<td>37.9 ± 10.1</td>
<td>2.6 ± 0.9</td>
<td>310 ± 123</td>
<td>0.88 ± 0.27</td>
<td>287 ± 165</td>
</tr>
<tr>
<td>Nov</td>
<td>265 ± 88</td>
<td>310.0 ± 15.4</td>
<td>18.0 ± 0.1</td>
<td>3.1 ± 2.8</td>
<td>39.4 ± 8.1</td>
<td>4.1 ± 1.5</td>
<td>776 ± 457</td>
<td>0.46 ± 0.02</td>
<td>363 ± 229</td>
</tr>
<tr>
<td>Dec</td>
<td>273 ± 123</td>
<td>347.5 ± 104.5</td>
<td>14.0 ± 1.1</td>
<td>3.1 ± 5.0</td>
<td>50.7 ± 12.7</td>
<td>4.7 ± 0.5</td>
<td>958 ± 785</td>
<td>0.52 ± 0.16</td>
<td>434 ± 257</td>
</tr>
</tbody>
</table>

* Mass concentrations (ng/m^3) of total n-alkanes were scaled to minimize the effect of variations in PBL height.

Table 2. Monthly average values of diagnostic parameters, used to assess biogenic and petrogenic source contributions in scaled total n-alkane concentrations.

<table>
<thead>
<tr>
<th>Month</th>
<th>Cmax</th>
<th>ACL</th>
<th>CPI</th>
<th>WNA% (Biogenic)</th>
<th>PNA% (Petrogenic)</th>
<th>Σ Biogenic n-Alkanes (ng/m^3)^2</th>
<th>Σ Petrogenic n-Alkanes (ng/m^3)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan</td>
<td>C31</td>
<td>30 ± 0.1</td>
<td>3.3 ± 0.8</td>
<td>54.5 ± 9.5</td>
<td>45.5 ± 9.5</td>
<td>185 ± 40</td>
<td>169 ± 99</td>
</tr>
<tr>
<td>Feb*</td>
<td>C29</td>
<td>29 ± 0.1</td>
<td>2.2 ± 0.5</td>
<td>41.1 ± 4.5</td>
<td>58.9 ± 4.5</td>
<td>910 ± 43</td>
<td>159 ± 72</td>
</tr>
<tr>
<td>Mar*</td>
<td>C29</td>
<td>28 ± 1.0</td>
<td>1.8 ± 0.5</td>
<td>31.9 ± 8.7</td>
<td>68.1 ± 8.7</td>
<td>56 ± 59</td>
<td>97 ± 66</td>
</tr>
<tr>
<td>Apr</td>
<td>C29</td>
<td>29 ± 0.1</td>
<td>2.9 ± 0.1</td>
<td>48.8 ± 2.7</td>
<td>51.2 ± 2.7</td>
<td>932 ± 576</td>
<td>1015 ± 712</td>
</tr>
<tr>
<td>May*</td>
<td>C29</td>
<td>29 ± 0.4</td>
<td>2.8 ± 0.0</td>
<td>47.9 ± 0.0</td>
<td>52.1 ± 0.0</td>
<td>539 ± 238</td>
<td>586 ± 259</td>
</tr>
<tr>
<td>Jun*</td>
<td>C29</td>
<td>30 ± 0.0</td>
<td>2.0 ± 0.5</td>
<td>32.9 ± 10.8</td>
<td>67.1 ± 10.8</td>
<td>208 ± 57</td>
<td>430 ± 95</td>
</tr>
<tr>
<td>Jul</td>
<td>C31</td>
<td>30 ± 0.1</td>
<td>2.8 ± 0.6</td>
<td>47.0 ± 7.8</td>
<td>53.0 ± 7.8</td>
<td>185 ± 66</td>
<td>204 ± 48</td>
</tr>
<tr>
<td>Aug</td>
<td>C29</td>
<td>30 ± 0.5</td>
<td>2.5 ± 0.6</td>
<td>46.7 ± 15.1</td>
<td>53.3 ± 15.1</td>
<td>205 ± 86</td>
<td>240 ± 106</td>
</tr>
<tr>
<td>Sep*</td>
<td>C29</td>
<td>29 ± 0.3</td>
<td>1.6 ± 0.4</td>
<td>31.0 ± 5.2</td>
<td>69.0 ± 5.2</td>
<td>63 ± 22</td>
<td>144 ± 56</td>
</tr>
<tr>
<td>Oct*</td>
<td>C29</td>
<td>29 ± 1.3</td>
<td>1.4 ± 0.3</td>
<td>21.9 ± 9.2</td>
<td>78.1 ± 9.2</td>
<td>70 ± 52</td>
<td>216 ± 116</td>
</tr>
<tr>
<td>Nov*</td>
<td>C27</td>
<td>29 ± 0.1</td>
<td>1.6 ± 0.2</td>
<td>27.3 ± 7.2</td>
<td>72.7 ± 7.2</td>
<td>108 ± 89</td>
<td>256 ± 140</td>
</tr>
<tr>
<td>Dec*</td>
<td>C29</td>
<td>28 ± 0.2</td>
<td>1.9 ± 0.1</td>
<td>34.2 ± 0.5</td>
<td>65.8 ± 0.5</td>
<td>148 ± 86</td>
<td>286 ± 171</td>
</tr>
</tbody>
</table>

* Mass concentrations (ng/m^3) of total n-alkanes were scaled to minimize the effect of variations in PBL height.

* Months showing significant differences between WNA% and PNA% on the basis of t-test (0.95).
concentration of total n-alkanes (C11−C35) was 517 ± 256 ng/m³ with a minimum monthly average concentration of 179 ± 142 ng/m³ occurring in March and maximum average concentration of 958 ± 785 ng/m³ in December (Table 1 and Fig. 1(A)). March is a month of seasonal transition, where ambient temperature of around 19.8 ± 5.3°C plays an important role, leading to an overall observed decline in the average concentration of total n-alkanes in this month. It is neither too low to have possible source emissions from biomass burning (a practice commonly used to keep warm during winter months), nor is too high to induce convective re-suspension of crustal material and road side dust. It is important to notice that average total n-alkane concentrations were higher than that reported from other urban locations (Table 3). However, total n-alkanes (C11−C35) concentrations observed in present study are in broad agreement with that reported by Chowdhury et al. (2007).

Total n-alkanes concentration (ng/m³) in a particular sample represents the total mass of n-alkanes present in the total volume of air available for their mixing. Thus any variation in mass concentration of n-alkanes (ng/m³) can be attributed to variation in total mass of n-alkanes and/or variation in the total volume of air available for their mixing; it is expected that total volume would be modulated by the changes in PBL height. It is reasonable to assume that stated volume change will be directly proportional to change in the PBL height. To minimize the effect of monthly variation in PBL height on estimated monthly average n-alkane concentrations, they were multiplied with Dilution correction factor (DCF). Respective month’s DCF is defined as a ratio of monthly average PBL height to annual average PBL height for the sampling location, and is expressed as:

$$DCF_{month} = \frac{Monthly\ average\ PBL}{Annual\ average\ PBL}$$

DCF scaled monthly average total n-alkanes mass concentrations are tabulated in Table 1 and the same is plotted in Fig. 1(B); minimum and maximum scaled monthly average total n-alkanes mass concentrations were registered in March (153 ± 125 ng/m³) and April (1947 ± 1288 ng/m³) respectively. Monthly variations in the DCF-scaled monthly average total n-alkanes mass concentrations reflect monthly variation in source emission profile by affecting the magnitude of influx or efflux of n-alkanes, i.e. as pose to the profile obtained from the month-by-month un-scaled average n-alkane concentrations.

It is interesting to note that PM10 load (µg/m³) and monthly average total n-alkane concentration (ng/m³) is high in April and May (spring) and during November to January (winter); correspondence between these two is apparent (Table 1 and Fig. 1(A)) on the basis of calculated Pearson’s correlation coefficient (0.84). PBL and T, on the other hand is high during April and May while low during November to January (Table 1); implying that increase in PM10 load and total n-alkanes concentration during winter months is more to do with lower PBL. Whereas, the increased concentrations during April and May, even with higher PBL, imply the enhanced activity of the contributing sources and of involved processes. This inference is also ascertained from the DCF-scaled monthly average total n-alkanes concentrations to account for variation in source emission profile. Scaled monthly average total n-alkanes concentrations were many folds higher in April and May as compared to that in November–January (Table 1 and Fig. 1(B)).

A close appraisal of Table 1 also reveals that months showing low total n-alkanes concentrations (June–October and March) can be divided in two groups on the basis of precipitation and its absence. March, September and October correspond to months having no precipitation and they fall under group 1; these months are marked with low source(s) emissions and having PBL height around annual average (672 ± 382). Monsoonal period, when precipitation is high is represented by months June-August fall under group 2; this period is marked with source emission around annual average and moderately higher PBL values.

**Mass Fraction of Total n-Alkanes in PM10 Load**

Large annual variation in the monthly average PM10 load (µg/m³) is evident, of which total n-alkanes constitute a very small fraction. To enable comparison between n-alkane estimates reported in different studies, n-alkane concentrations are expressed as mass-fraction (ppm) in respective PM10 samples. This normalization also facilitates the comparison of n-alkane variation between the seasons, independent of the large variability present in the PM10 load. Normalized values of n-alkanes (ppm) are given in Table 1 and plotted in Fig. 1(C). Annual n-alkane average was 4368 ± 2067 ppm; minimum value was observed in October (1693 ± 1012), and maximum in July (8426 ± 674). Overall the major sources of PM10 aerosols over Delhi can be classified as: (1) Vehicular/Industrial Emissions and Biomass Burning (2) Materials of Crustal Origin (3) Wind-transported Dust from adjoining areas (4) Re-suspension of Road Dust. (Yadav and Rajamani, 2006; Srivastava et al., 2007; Tandon et al., 2008, 2010). Dust-storms, with decreasing frequencies from April to June, affect the particulate load’s characteristic as an additional factor during this period. These events not only assist the wind-transport of crustal material from adjoining regions of Rajasthan and Haryana, but also helps in the re-suspension of the local crustal material, road dust and soil having decomposed/fresh litter (Yadav and Rajamani, 2006). This results in high PM10 aerosol (µg/m³) and associated n-alkane load (ng/m³) in the month of April, which decreases by July. In this study, we observed that the fraction of n-alkanes (ppm) in PM10 increases from April to July: possible explanation could be the dilution effect caused by the crustal material on n-alkanes proportion in total PM10 load, and the decrease in strength of this dilution effect follows accordingly from April to July. Most of the crustal material constitutes coarser fraction of PM10 aerosols, whereas n-alkanes are generally present in the finer size fractions (Kadowaki et al., 1994), this factor along with the differences in the hydrophilic and hydrophobic properties of the crustal material and n-alkanes might lead to their differential life-times and rates of dry and wet deposition. This explains observed highest value of n-alkanes fraction in the month of July in present study.
However, from November to February, the values of PM$_{10}$ load (μg/m$^3$), $n$-alkanes concentration (ng/m$^3$) and $n$-alkanes fraction (ppm) show almost similar profile. This might be because during winter months, low temperature and low planetary boundary layer reduces the convective re-suspension of crustal material, road dust and soil; whereas, large scale biomass and refuse burning for heating purposes is a common practice in the region leading to high PM$_{10}$ load (μg/m$^3$), $n$-alkanes concentration (ng/m$^3$), and high $n$-alkanes fraction (ppm). Overall, on yearly basis we observe a negative relationship ($r = -0.72$) between the PM$_{10}$ concentration and $n$-alkanes fraction.
Distribution Profile of \( n \)-Alkanes (C\(_{11}\) to C\(_{35}\))

In Figs. 2(A–L), we have plotted the monthly average values of individual \( n \)-alkane (C\(_{11}\) to C\(_{35}\)) concentration (ng/m\(^3\)) along with the fractions originated from Plant Waxes and Petroleum combustion. As the concentrations of individual \( n \)-alkane species in the aerosol are important for this work, we have provided their monthly average concentrations (ng/m\(^3\)) in Table 4. Higher molecular weight \( n \)-alkanes with a predominance of odd carbon number congeners like C\(_{27}\), C\(_{29}\), C\(_{31}\) and C\(_{33}\) indicate biogenic contributions, whereas \( n \)-alkanes originating from petroleum sources do not show any such predominance. On the other hand, lower \( n \)-alkanes with maxima at C\(_{20}\), C\(_{23}\) and C\(_{25}\) signify petrogenic contributions (Simoneit, 1989; Rogge et al., 1993c). Among individual \( n \)-alkanes, abundance was mainly contributed by C\(_{25}\) to C\(_{31}\) alkanes. A typical saw tooth pattern of higher \( n \)-alkanes (C\(_{25}\)–C\(_{31}\)), with a predominance of odd carbon numbered congeners C\(_{27}\), C\(_{29}\) and C\(_{31}\) was found in our study, this concentration pattern representing higher molecular weight \( n \)-alkanes acts as a marker compound assemblage to identify contributions arising from natural sources (plant litter from garden soil, road dust) and anthropogenic activities (smoking, gardening, biomass burning), which redistributes plant waxes (Rogge et al., 1993c). Similar predominance of odd carbon numbered congeners was found by Kadowaki (1994); Cheng et al. (2006) and Kotianová et al. (2008) (Table 3).

Monthly and Seasonal Variations in the Source(s) Contribution(s) of \( n \)-Alkanes

In an urban environment, there can be many sources responsible for \( n \)-alkanes release into the atmosphere. Anthropogenic sources typically include the combustion of fossil fuels and biomass burning. Whereas, biogenic sources include particles shed from the epicuticular waxes of vascular plants and direct suspension of pollen, microorganisms etc. (Rogge et al., 1993c). In addition, re-suspension of road dust and garden soil also injects \( n \)-alkanes representing mixed origin. In Table 2, we have listed monthly average values along with associated standard deviation in estimated \( n \)-alkane based diagnostic parameters (ACL, Cmax, CPI and WNA%). Table 2, also provides DCF-scaled monthly average concentrations, corrected for annual variations in PBL, of total \( n \)-alkanes originated from Biogenic and from petrogenic sources.

Calculated C\(_{\text{max}}\) in most of the months was at C\(_{29}\) \( n \)-alkane, in few months at C\(_{27}\) (October and November) and at C\(_{31}\) in January and July. C\(_{\text{max}}\) value at C\(_{29}\) is a signature for the \( n \)-alkanes arising from road dust, containing accumulated automobile and industrial emissions, and surface deposited plant litter mix, while C\(_{31}\) stands as a major homologue for leaf abrasion products (Rogge et al., 1993c). Average chain length (ACL) for \( n \)-alkanes varied from 30 ± 0.1 (maximum) to 28 ± 1.0 (minimum) with the mean annual value of 29 ± 1 (Table 2); little variation in this index imply biogenic activities from uniform plant-type varieties as the source of \( n \)-alkanes (Jeng, 2006).

Annual average CPI value was 2.2 ± 0.6, however it varied from minimum of 1.4 ± 0.3 in October to a maximum in
Fig. 2. Source contributions from Wax n-alkane (WNA) and Petroleum n-alkane (PNA) concentration in individual n-alkanes (C11–C35), with WNA%, PNA% and CPI in total n-alkanes.

January (3.3 ± 0.8). Similarly the annual mean WNA% stood at 39 ± 10%, and varied from 22 ± 9% in October to 55 ± 10% in January. CPI results were in correspondence with the study done by Cheng et al. (2006), where CPI varied from 1.14 to 2.38, while WNA% contributions showed similar variations as reported by Young and Wang, 2002 for Taipei city, where they showed up to 31% contributions from plant waxes (Table 3). Annual mean values of CPI and WNA% suggest petrogenic inputs (61 ± 10%) to be the dominant source of organic aerosols in the region, with spurts of increased biogenic influences (Alves et al., 2009). As reported earlier (Zheng et al., 2000), excellent positive correlation between CPI and WNA% ($R^2 = 0.96$) was observed.

In winter months - December-January-February (DJF) - CPI values varied between 1.9 ± 0.1 and 3.3 ± 0.8, and WNA% between 34 ± 0.5 and 55 ± 9.5. Maximum annual CPI value of 3.3 ± 0.8 coincided well with the annual maximum WNA% value of 55 ± 10 (recorded in January). On the other hand, maxima for ACL and $C_{\text{max}}$ were 30.0 ± 1.0 and 31, respectively in January; it follows that though petrogenic sources are the dominant contributor (58%) in winter season, but significant percentage of aerosol associated n-alkanes (42%) also originates from biological sources (Table 2 and Figs. 2(A–C)), which can be attributed to biomass burning (Simonet, 2002), a common prevalent practice in winter months used for heating in this region.

CPI values 1.8 ± 0.5–2.9 ± 0.1 and WNA% 32 ± 8.7–49 ± 2.7 were observed for spring months; March-April-May (MAM). High CPI values and WNA% in this season, suggest almost equal contribution of petrogenic (53%) and biogenic (47%) sources to aerosol associated n-alkanes (Table 2 and Figs. 2(D-F)). In this season, enhanced emission of pollens and epicuticular waxes from other plant parts is common, which may further be enhanced by convection or dust storm assisted re-suspension of the soil containing dry-degraded plant organic matter (Simoneit, 2002; Singh et al., 2003; Tandon et al., 2008). Direct suspension of crystalline epicuticular wax protrusions from the leaf surfaces during spring season is also assisted by wind abrasion and, sandblasting effect (Percy et al., 1994; Schefuß et al., 2003) to enhance the n-alkanes fraction in PM$_{10}$ (Rogge et al., 1993c).

In summer (monsoon) months - June-July-August (JJA) - CPI values varied between 2.0 ± 0.5 and 2.8 ± 0.6, and WNA% ranged between 33 ± 10.8 and 47 ± 15.1. These diagnostic tools again emphasize that petrogenic sources are the dominant contributor (59%) in summer (monsoon)
<table>
<thead>
<tr>
<th>n-Alkane species</th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>Jun</th>
<th>July</th>
<th>Aug</th>
<th>Sep</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
</tr>
</thead>
<tbody>
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<td>Undecane</td>
<td>0.9 ± 1.6</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.1 ± 1.6</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>n.d.</td>
<td>0.4 ± 0.7</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.1 ± 1.5</td>
<td>0.3 ± 0.1</td>
<td>0.2 ± 0.4</td>
<td>n.d.</td>
<td>0.1 ± 0.1</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Pentadecane</td>
<td>0.5 ± 0.5</td>
<td>n.d.</td>
<td>0.3 ± 0.2</td>
<td>0.4 ± 0.0</td>
<td>0.2 ± 0.1</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.2 ± 0.2</td>
<td>0.4 ± 0.1</td>
<td>0.3 ± 0.6</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>n.d.</td>
<td>0.2 ± 0.3</td>
<td>n.d.</td>
<td>0.6 ± 0.8</td>
<td>n.d.</td>
<td>0.1 ± 0.2</td>
<td>0.2 ± 0.4</td>
<td>0.00</td>
<td>0.2 ± 0.2</td>
<td>n.d.</td>
<td>13.2 ± 18.4</td>
<td>4.9 ± 6.9</td>
</tr>
<tr>
<td>Heptadecan</td>
<td>0.3 ± 0.6</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.5 ± 0.7</td>
<td>n.d.</td>
<td>0.7 ± 0.9</td>
<td>0.8 ± 0.2</td>
<td>0.6 ± 1.1</td>
<td>0.6 ± 0.8</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Octadecane</td>
<td>0.3 ± 0.5</td>
<td>0.5 ± 0.9</td>
<td>0.3 ± 0.4</td>
<td>2.7 ± 3.9</td>
<td>1.8 ± 0.4</td>
<td>0.6 ± 0.5</td>
<td>0.7 ± 0.2</td>
<td>0.9 ± 1.2</td>
<td>1.9 ± 1.4</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Nonadecane</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.4 ± 0.6</td>
<td>0.2 ± 0.4</td>
<td>n.d.</td>
<td>1.0 ± 1.4</td>
<td>5.5 ± 7.8</td>
<td>n.d.</td>
</tr>
<tr>
<td>Eicosane</td>
<td>0.6 ± 0.6</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.4 ± 0.6</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>7.9 ± 11.1</td>
</tr>
<tr>
<td>Heneicosane</td>
<td>0.2 ± 0.4</td>
<td>0.8 ± 0.7</td>
<td>1.9 ± 1.0</td>
<td>8.8 ± 12.5</td>
<td>5.3 ± 0.2</td>
<td>0.4 ± 0.2</td>
<td>0.3 ± 0.3</td>
<td>7.5 ± 6.3</td>
<td>3.1 ± 1.8</td>
<td>6.3 ± 2.5</td>
<td>14.0 ± 1.3</td>
<td>n.d.</td>
</tr>
<tr>
<td>Docosane</td>
<td>2.9 ± 2.4</td>
<td>0.7 ± 1.2</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>18 ± 3.0</td>
<td>0.3 ± 0.6</td>
<td>1.1 ± 1.4</td>
<td>6.6 ± 9.4</td>
<td>n.d.</td>
</tr>
<tr>
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<td>0.8 ± 0.7</td>
<td>0.3 ± 0.2</td>
<td>0.8 ± 0.3</td>
<td>9.8 ± 1.6</td>
<td>1.4 ± 0.7</td>
<td>0.7 ± 0.1</td>
<td>0.2 ± 0.1</td>
<td>0.5 ± 0.8</td>
<td>0.5 ± 0.4</td>
<td>1.9 ± 1.3</td>
<td>8.9 ± 2.6</td>
<td>12.8 ± 8.7</td>
</tr>
<tr>
<td>Tetracosane</td>
<td>3.5 ± 0.7</td>
<td>1.7 ± 1.6</td>
<td>1.4 ± 1.2</td>
<td>3.0 ± 4.3</td>
<td>n.d.</td>
<td>0.8 ± 1.1</td>
<td>0.4 ± 0.7</td>
<td>n.d.</td>
<td>0.1 ± 0.2</td>
<td>3.6 ± 2.9</td>
<td>16.2 ± 5.1</td>
<td>n.d.</td>
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<tr>
<td>Pentacosane</td>
<td>8.1 ± 2.3</td>
<td>6.5 ± 3.8</td>
<td>4.5 ± 0.9</td>
<td>26.9 ± 16.4</td>
<td>7.2 ± 1.4</td>
<td>2.8 ± 3.9</td>
<td>0.7 ± 1.2</td>
<td>2.3 ± 2.1</td>
<td>1.7 ± 1.2</td>
<td>14.2 ± 5.6</td>
<td>44.9 ± 12.5</td>
<td>53.5 ± 36.6</td>
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<tr>
<td>Hexacosane</td>
<td>9.2 ± 8.4</td>
<td>13.2 ± 9.0</td>
<td>12.2 ± 6.0</td>
<td>51.6 ± 27.9</td>
<td>14.4 ± 1.2</td>
<td>4.3 ± 6.1</td>
<td>3.3 ± 2.9</td>
<td>4.2 ± 4.4</td>
<td>6.8 ± 1.7</td>
<td>34.5 ± 11.5</td>
<td>92.9 ± 23.2</td>
<td>75.3 ± 62.6</td>
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<td>Heptacosane</td>
<td>21.8 ± 22.9</td>
<td>37.0 ± 19.9</td>
<td>28.2 ± 6.3</td>
<td>122.6 ± 63.3</td>
<td>49.0 ± 16.0</td>
<td>17.6 ± 2.2</td>
<td>10.6 ± 0.9</td>
<td>13.8 ± 13.5</td>
<td>21.4 ± 6.9</td>
<td>73.5 ± 38.2</td>
<td>195.3 ± 118.5</td>
<td>171.5 ± 126.7</td>
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<tr>
<td>Octacosane</td>
<td>29.5 ± 18.5</td>
<td>41.6 ± 22.0</td>
<td>18.4 ± 3.4</td>
<td>105.6 ± 47.6</td>
<td>50.1 ± 13.0</td>
<td>30.2 ± 3.4</td>
<td>18.4 ± 1.6</td>
<td>26.7 ± 7.0</td>
<td>29.6 ± 9.7</td>
<td>46.1 ± 35.1</td>
<td>119.1 ± 119.4</td>
<td>169.3 ± 131.8</td>
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<tr>
<td>Nonacosane</td>
<td>193.7 ± 94.4</td>
<td>193.5 ± 47.7</td>
<td>60.5 ± 73.5</td>
<td>402.9 ± 94.0</td>
<td>252.6 ± 37.1</td>
<td>155.2 ± 6.5</td>
<td>96.2 ± 12.9</td>
<td>144.9 ± 15.4</td>
<td>111.2 ± 30.2</td>
<td>63.6 ± 74.4</td>
<td>127.2 ± 155.6</td>
<td>340.8 ± 301.2</td>
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<td>Tricontane</td>
<td>142.4 ± 99.5</td>
<td>44.0 ± 38.2</td>
<td>26.3 ± 39.0</td>
<td>51.7 ± 15.4</td>
<td>71.9 ± 46.1</td>
<td>94.7 ± 19.0</td>
<td>63.7 ± 3.5</td>
<td>62.2 ± 50.9</td>
<td>53.2 ± 23.7</td>
<td>17.2 ± 23.1</td>
<td>n.d.</td>
<td>62.4 ± 64.6</td>
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<td>Hentriacontane</td>
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<td>61.9 ± 11.8</td>
<td>23.0 ± 39.9</td>
<td>36.8 ± 20.0</td>
<td>73.8 ± 72.8</td>
<td>103.0 ± 21.3</td>
<td>135.7 ± 44.1</td>
<td>129.0 ± 76.3</td>
<td>151.1 ± 13.4</td>
<td>3.3 ± 4.1</td>
<td>38.2 ± 16.3</td>
<td>49.1 ± 45.9</td>
</tr>
<tr>
<td>Dotriacontane</td>
<td>10.2 ± 9.1</td>
<td>39.9 ± 69.1</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.4 ± 2.5</td>
<td>21.9 ± 34.7</td>
<td>9.4 ± 18.7</td>
<td>6.3 ± 5.3</td>
<td>18.5 ± 3.45</td>
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<tr>
<td>Triotriacontane</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.7 ± 1.3</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>10.9 ± 10.7</td>
<td>28.4 ± 16.6</td>
<td>1.2 ± 1.7</td>
</tr>
</tbody>
</table>

n.d.: not detected
season, though significant percentage of aerosol associated \(n\)-alkanes (41%) also originate from biological sources (Table 2 and Figs. 2(G–I)), Monsoon rains and high humidity, during this season supports the spurt in biological growth of vegetation.

CPI variation from 1.4 ± 0.3 to 1.6 ± 0.4 and WNA% from 22 ± 9.2 to 31 ± 5.2 were observed during autumn (post monsoon) months - September-October-November (SON). These observations (Table 2 and Figs. 2(J–L)), indicate a typical urban environment where dominant inputs of aerosol associated \(n\)-alkanes arise from petrogenic (vehicular and industrial) emissions (72%), and to a lesser extent from biogenic activities (28%).

Seasonal variations in the mass concentrations, scaled for annual variations in PBL, of total \(n\)-alkanes, arising from petrogenic and biogenic sources are shown in Figs. 3(A–D). As discussed in section 3.1, this scaling minimizes the effect of monthly PBL height variations, the changes in scaled values can solely be attributed to changes in source emissions. Maximum contributions were observed during spring months (Fig. 3(B)), when frequent dust storms occur in this region, which transport large amount of dust from adjacent areas in addition to large scale resuspension of local road dust and garden soils. These resuspended road dust and garden soils have a mixed character in terms of \(n\)-alkanes origin (Rogge et al., 1993c). Little variation was observed in source emissions originating from petrogenic sources [205 ng/m\(^3\) in autumn and winter - 291 ng/m\(^3\) in summer (monsoon) months], whereas, large variation was noted in source emissions arising from biogenic sources [80 ng/m\(^3\) in autumn - 199 ng/m\(^3\) in summer (monsoon) months] (Figs. 3(A, C and D)).

**CONCLUSIONS**

Significant seasonal variations were observed, both, in mass concentrations and mass fractions of total \(n\)-alkanes \((C_{11}-C_{35})\). Analysis of results indicate strong positive correlation \((r = 0.84)\) between \(PM_{10}\) load \((\mu g/m^3)\) and mass concentrations of total \(n\)-alkane \((ng/m^3)\); whereas, negative correlation \((r = -0.72)\) was observed between \(PM_{10}\) load and mass fractions of total \(n\)-alkanes \((ppm)\). Findings suggest that high total \(n\)-alkanes concentration during winter months can be attributed to lower PBL height, whereas the same during spring was linked with enhanced activity of the contributing sources and processes. Among individual \(n\)-alkanes, the abundance was mainly contributed primarily by \(C_{23}\) to \(C_{31}\) \(n\)-alkanes. Calculated annual average CPI value was 2.2 ± 0.6, and annual mean WNA% stood at 39 ± 10%, and an excellent positive correlation was observed between CPI and WNA% \((R^2 = 0.96)\). Annual mean values of CPI and WNA% imply petrogenic inputs (61 ± 10%) to be the dominant source of \(n\)-alkanes in \(PM_{10}\).

Significant seasonal variations in the source profile of aerosol associated \(n\)-alkanes were observed. Established diagnostic parameters indicated that for autumn months dominant inputs of aerosol associated \(n\)-alkanes arise from petrogenic (vehicular and industrial) emissions (72 ± 7%) and lesser proportion from biogenic activities (28 ± 7%). In other seasons, though petrogenic sources remained a dominant contributor (53 ± 6%–59 ± 14%), but the contributions originating from biological sources— involving varying processes— were also comparable (41 ± 14%–47 ± 6%). It was interesting to note that the emissions of total \(n\)-alkanes from both petrogenic and biogenic sources were at their

![Fig. 3](image_url)  
**Fig. 3.** Seasonal pattern of biogenic and petrogenic source contributions in scaled total \(n\)-alkane concentrations.
maximum in spring months, i.e., much higher than observed in other months. In rest of the months, small variation was observed in the emissions of total n-alkanes from petrogenic sources, whereas large variation was noted in the emissions of total n-alkanes arising from biogenic sources.

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