Chapter 5

Variations in Light

$(C_1-C_5)$ Hydrocarbons at Nainital and Indo-Gangetic Plain

Hydrocarbons (methane and non-methane) play very important role in the atmospheric chemistry in particular related with the formation of tropospheric ozone [e.g. Crutzen, 1995; Atlas and Ridley, 1996; Atkinson, 2000; Kleinman et al., 2005]. The lifetime of $CH_4$ is altered through changes in the OH concentration, leading to change in tropospheric ozone. The hydroxyl radical provides a dominant sink for many greenhouse gases including $CH_4$ [IPCC, 2007]. The ozone production due to methane is still uncertain [IPCC, 2007] and the 100-year Global Warming Potential (GWP) for methane is reported to be increased from 23 in the TAR to 25 [IPCC, 2007]. Additionally, the dependence of ozone production on non-methane
hydrocarbons (NMHCs) is nonlinear and very complex [Brasseur et al., 1999b]. Also, the ozone production potential for NMHCs is much higher (10–13) [Chameides, 1988]. Oxidation of NMHCs leads to the production of ozone, which depends on the NO\textsubscript{x} mixing ratios. NMHCs also contribute to global atmospheric CO and some of the NMHCs can be used as a tracer of atmospheric transport. Moreover, some of the anthropogenic as well as biogenic hydrocarbons also act as the precursors for the Secondary Organic Aerosols (SOA), accounting for considerable fraction of the aerosol budget in the troposphere [Kanakidou et al., 2005; Kroll and Seinfeld, 2008]. Therefore, the measurements of NMHCs are essential for characterizing the ozone pollution [Chameides and Walker, 1973; Crutzen, 1973]. Despite of this, the systematic measurements of NMHCs are nearly non-existing over the central Himalayas and the Indo-Gangetic plain regions.

It has been shown in the chapter 3 that ozone levels at Nainital are similar to other high altitude locations around the globe, however; in contrast, the levels of CO and NO\textsubscript{y} are moderately higher at Nainital. This clearly indicates that the tropospheric chemistry of ozone is different / complex over this region and needs more detailed investigation particularly of the role of non-methane hydrocarbons.

In this direction, analysis of air samples from Nainital and two sites from IGP region has been initiated. Nainital is at unique location and its remoteness from any direct anthropogenic influences, can provide invaluable signatures of clean free tropospheric background, regional pollution, long-range transport and marine air masses. The regular sampling measurements at Nainital are further supplemented with the collection and analysis of air samples from two nearby sites (20–40 km from Nainital) in the Haldwani and Pantnagar located in the semi-urban environment of the Indo-Gangetic Plain (IGP) (Figure 5.1). The general
meteorological conditions such as solar radiation, temperature, rainfall, and synoptic winds over this region have been presented in the Chapter 3 and can also be seen in a previous paper presenting surface ozone analysis at Pantnagar in the IGP [Ojha et al., 2012].

![Google Earth image showing the topography around Nainital](image)

**Figure 5.1:** A Google Earth image showing the topography around Nainital (white triangle) site. Locations of Haldwani and Pantnagar (square symbol) sites are also shown.

Hydrocarbons can be gases (e.g. methane, propane), liquids (e.g. hexane, benzene) and waxes or low melting solids (e.g. paraffin wax and naphthalene). Here, we have used the alkanes, alkenes and alkynes. The general chemical formula of alkanes is \( \text{C}_n\text{H}_{2n+2} \) and they are saturated hydrocarbons; consist only of hydrogen and carbon atoms, in which all bonds are single bonds. The simplest alkane is methane (\( \text{CH}_4 \)). Alkanes have strong inter-molecular van der waals forces, consequently greater
boiling points. Also, larger the molecule higher the melting point. The general chemical formula of alkenes is \( \text{C}_n\text{H}_{2n} \). Alkene or olefin is an unsaturated chemical compound, in which two neighboring carbon atoms share a pair of electrons, called as a double bond (e.g. ethene, propene, butane). The simplest alkene is ethene/ethylene (\( \text{C}_2\text{H}_4 \)). Alkenes are relatively stable compounds, but are more reactive than alkanes due to the presence of a carbon-carbon pi bond. Similarly to alkenes, alkyne is also an unsaturated hydrocarbon, which has at least one carbon-carbon triple bond. The general chemical formula of alkynes is \( \text{C}_n\text{H}_{2n-2} \). The dominant alkyne is acetylene or formally known as ethyne (\( \text{C}_2\text{H}_2 \)). Most of the other industrially useful alkyne is prepared from acetylene, through condensation with formaldehyde. Alkynes are also hydrophobic like other hydrocarbons and tend to be more reactive.

The analysis of 3-year long (April 2009-December 2011) datasets of \( \text{CH}_4 \) and NMHCs from Nainital is being presented for the first time. Methane (\( \text{CH}_4 \)) observations are not available for few months after July 2011. Air samples were collected systematically with a frequency of 3 samples per week on every Monday, Wednesday and Friday at 1430 hours (IST). This time is chosen to sample the convectively well mixed air masses considering the evolution of the planetary boundary layer during afternoon (Chapter 3). The samples have been analyzed to measure light hydrocarbons including methane (\( \text{CH}_4 \)), ethane (\( \text{C}_2\text{H}_6 \)), ethene (\( \text{C}_2\text{H}_4 \)), propane (\( \text{C}_3\text{H}_8 \)), i-butane (\( i\text{-C}_4\text{H}_{10} \)), n-butane (\( n\text{-C}_4\text{H}_{10} \)), acetylene/ethyne (\( \text{C}_2\text{H}_2 \)) and i-pentane (\( i\text{-C}_5\text{H}_{12} \)) using GC. Details of observation techniques are provided in Chapter-2.
The time series of CH$_4$, C$_2$-C$_5$ NMHCs observations for the complete study period are shown in Figure 5.2, 5.3 and 5.4 respectively.

**Figure 5.2:** The time series of CH$_4$ observations at Nainital during April 2009 to July 2011. The error bars represent the standard deviation (1-sigma).
Figure 5.3: The time series of (a) ethane, (b) ethene, (c) propane, and (d) propene observations at Nainital during 2009-2011 period.
The average CH$_4$ values were observed to be the maximum during January 2011 (1.97±0.09 ppmv) and minimum during May 2009 (1.75±0.07 ppmv). During the year 2010 and 2011 average CH$_4$ values are in the range of 1.77-1.91 ppmv and 1.77-1.97 ppmv respectively. The daily CH$_4$ observations (all data) show larger variability with levels reaching up to 2.2 ppmv. The average values of ethane, ethene, propane, propene, $i$-butane, acetylene, $n$-butane and $i$-pentane are observed to be in the ranges of 0.81-3.08 ppbv, 0.22-1.69 ppbv, 0.17-1.32 ppbv, 0.13-1.62 ppbv, 0.11-1.25 ppbv, 0.16-1.63 ppbv, 0.29-2.33 ppbv and 0.11-1.51 ppbv respectively during the study period. The maximum values of ethane, ethene, propane, propene, $i$-butane, acetylene, $n$-butane and $i$-pentane during the study period are observed to be 3.18±1.21, 1.69±1.04, 1.32±1.4, 1.62±0.91, 1.25±0.58, 1.63±1.51, 2.33±1.87 and 1.51±1.42 ppbv respectively. While, the minimum values of ethane, ethene, propane, propene, $i$-butane, acetylene, $n$-butane and $i$-pentane during the whole study period are observed to be 0.54±0.3, 0.22±0.1, 0.17±0.18, 0.13±0.07, 0.11±0.22, 0.12±0.02, 0.29±0.11 and 0.11±0.04 ppbv respectively.
Figure 5.4: The time series of the (a) i-butane, (b) acetylene, (c) n-butane, and (d) i-pentane observations at Nainital during April 2009 to December 2011 period.
The shorter-lived gases e.g. propane, i-butane, n-butane and acetylene peak are seen to exhibit longer periods of low summer values. The levels of short-lived n- and i-butanes (summer lifetimes of 5.5-5.7 days) [Swanson et al., 2003] drop quickly during May, and by July their mixing ratios are below 0.2 ppbv and 0.1 ppbv. Thus, their low summer levels are attained the earliest and last longest. The medium lived species such as propane and acetylene (summer lifetimes of 14-19 days) reach low levels of about 60 pptv and 80 pptv respectively in early June. Average concentrations being reported for Nainital are suggested to represent the background variations influenced by transport from nearby low altitude sources (IGP), chemical lifetime and their dilution.

The seasonal variations in the measured hydrocarbons and the analysis of inter-species correlations are discussed in detail in the following sections:

5.1. Seasonal Variations

5.1.1. Seasonal Variations in CH$_4$ and C$_2$-C$_5$ NMHCs at Nainital

Seasonal variation in CH$_4$ and NMHCs (C$_2$-C$_5$) at Nainital are shown in the Figure 5.5 and 5.6 for 2009-2011 period. Monthly average values of all the measured hydrocarbons are given in the Table 5.1. Monthly average CH$_4$ at Nainital shows an increase in the levels (1.86-1.88 ppmv) during post-monsoon (Figure 5.5). Methane levels remain higher during winter. Methane levels start decreasing towards March and become lowest during summer-monsoon (1.79±0.07 ppmv). The post-monsoon enhancement in methane is mainly attributed to the growth of rice in the agricultural regions of the northern India (Punjab, Haryana). The back air trajectories show
transport of northern hemispheric air masses during winter, which could be rich in methane [Ganesan et al., 2013]. In addition to the rice agriculture, methane emissions also result from cattle farming and biomass burning [Neue, 1993; Subak, 1994; Ruddiman, 2003]. Air masses from Uttar Pradesh, one of the top five methane emitter states in India, [Garg et al., 2011], could also influence the levels over Nainital. The methane emissions in India have been reported to grow since 1985, from 18.85 Tg to 20.56 Tg in 2008 [Garg et al., 2011].

![Box plot showing the seasonal variation in methane at Nainital during 2009-2011 period. The blue and black solid lines inside the box indicate mean and median values respectively. The whiskers below and above are 10th and 90th percentiles and the 5th and 95th outliers are shown by filled circles.](image)

**Figure 5.5:** Box plot showing the seasonal variation in methane at Nainital during 2009-2011 period. The blue and black solid lines inside the box indicate mean and median values respectively. The whiskers below and above are 10th and 90th percentiles and the 5th and 95th outliers are shown by filled circles.

The methane emission rates from paddy fields as estimated globally is reported to be 40 Tg yr\(^{-1}\) [Sass et al., 1999] which accounts for about 6% of the total methane...
emissions [IPCC, 2001]. Anthropogenic origin of methane emissions accounts for about 50% of the global annual methane emissions, while, irrigated rice cultivation could account for up to 12% of this flux [IPCC, 2007]. Estimates of methane emissions from rice fields, made recently, varies between 39-112 Tg CH₄ yr⁻¹ [Denman et al., 2007]. The global emission of methane for the year 2000 was calculated by Yan et al., 2009 and is reported to be 25.6 Tg a⁻¹. In warm weather conditions, and water-logged soil, rice paddies acting as wetlands emit significant amount of methane. It has been studied that average methane flux during the growing season is significantly affected by number of factors such as water management, soil pH, and climate [Yan et al., 2005]. Furthermore, since methane is a long-lived species, having a lifetime of 9-10 yrs [Prinn et al., 1995], therefore, it can also be transported from distant sources in addition to the nearby source regions.

Seasonal variations in ethane, ethene, propane, propene, i-butane, acetylene, n-butane and i-pentane are shown in figure 5.6 and their monthly average values are shown in Table 5.1. All the species discern pronounced seasonal variations at Nainital except i-butane and i-pentane. Most of the NMHCs (C₂-C₅) show winter maxima and summer-monsoon minima at Nainital, which is observed to be similar to previous studies in the Northern Hemisphere (e.g. Harvard Forest, Central Massachusetts; Pallas, Scandinavia; MLO, US; Mt. Abu, India; Summit, Greenland; Pico Mountain, Azores; Durham, New Hampshire, US; Mace Head, Ireland) [Goldstein et al., 1995; Laurila and Hakola, 1996; Greenberg et al., 1996; Swanson et al., 2003; Sahu and Lal, 2006; Helmig et al., 2008; Yates et al., 2010; Russo et al., 2010; Russo et al., 2011; Derwent et al., 2012].
Table 5.1: Monthly Average values of CH$_4$ and C$_2$-C$_5$ light non-methane hydrocarbons with 1-Sigma Standard Deviation, at Nainital, where n denotes the no. of samples analyzed. Methane (CH$_4$) values are in ppmv and non-methane hydrocarbons are in ppbv.

<table>
<thead>
<tr>
<th>Month</th>
<th>No. of Samples methane</th>
<th>No. of Samples NMHCs</th>
<th>Methane (n)</th>
<th>Ethane (n)</th>
<th>Ethene (n)</th>
<th>Propane (n)</th>
<th>Propene (n)</th>
<th>i-butane (n)</th>
<th>Acetylene (n)</th>
<th>n-butane (n)</th>
<th>i-pentane (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan</td>
<td>22</td>
<td>20</td>
<td>1.89±0.10 (22)</td>
<td>1.86±0.71 (18)</td>
<td>0.72±0.62 (19)</td>
<td>0.67±0.69 (16)</td>
<td>1.28±1.22 (9)</td>
<td>0.75±0.76 (15)</td>
<td>0.99±1.20 (16)</td>
<td>1.67±1.23 (18)</td>
<td>0.93±0.93 (15)</td>
</tr>
<tr>
<td>Feb</td>
<td>14</td>
<td>14</td>
<td>1.86±0.07 (14)</td>
<td>2.72±0.84 (14)</td>
<td>0.93±0.64 (14)</td>
<td>0.96±1.05 (9)</td>
<td>0.66±0.52 (7)</td>
<td>0.56±0.46 (10)</td>
<td>0.91±0.89 (10)</td>
<td>1.69±0.96 (10)</td>
<td>0.40±0.29 (10)</td>
</tr>
<tr>
<td>Mar</td>
<td>27</td>
<td>28</td>
<td>1.85±0.08 (27)</td>
<td>2.38±0.85 (28)</td>
<td>0.79±0.51 (27)</td>
<td>0.39±0.27 (23)</td>
<td>0.27±0.22 (15)</td>
<td>0.27±0.14 (25)</td>
<td>0.34±0.17 (24)</td>
<td>1.41±0.66 (24)</td>
<td>0.41±0.41 (26)</td>
</tr>
<tr>
<td>Apr</td>
<td>32</td>
<td>29</td>
<td>1.80±0.05 (32)</td>
<td>2.34±0.99 (29)</td>
<td>0.92±0.78 (29)</td>
<td>0.38±0.52 (25)</td>
<td>0.49±0.46 (12)</td>
<td>0.24±0.36 (19)</td>
<td>0.24±0.28 (23)</td>
<td>0.96±0.54 (28)</td>
<td>0.20±0.14 (23)</td>
</tr>
<tr>
<td>May</td>
<td>39</td>
<td>41</td>
<td>1.77±0.05 (39)</td>
<td>1.74±0.39 (40)</td>
<td>0.54±0.38 (41)</td>
<td>0.30±0.33 (36)</td>
<td>0.28±0.53 (28)</td>
<td>0.25±0.31 (31)</td>
<td>0.30±0.45 (34)</td>
<td>0.69±0.34 (41)</td>
<td>0.28±0.32 (38)</td>
</tr>
<tr>
<td>Jun</td>
<td>38</td>
<td>38</td>
<td>1.80±0.06 (37)</td>
<td>1.50±0.40 (38)</td>
<td>0.46±0.34 (37)</td>
<td>0.36±0.39 (25)</td>
<td>0.25±0.24 (22)</td>
<td>0.40±0.54 (27)</td>
<td>0.32±0.34 (30)</td>
<td>0.67±0.48 (36)</td>
<td>0.34±0.37 (28)</td>
</tr>
<tr>
<td>Jul</td>
<td>32</td>
<td>37</td>
<td>1.78±0.07 (32)</td>
<td>0.86±0.23 (36)</td>
<td>0.27±0.18 (36)</td>
<td>0.21±0.24 (14)</td>
<td>0.38±0.68 (20)</td>
<td>0.37±0.53 (25)</td>
<td>0.30±0.35 (25)</td>
<td>0.43±0.42 (34)</td>
<td>0.30±0.39 (26)</td>
</tr>
<tr>
<td>Aug</td>
<td>22</td>
<td>34</td>
<td>1.81±0.07 (22)</td>
<td>1.04±0.40 (31)</td>
<td>0.58±1.15 (34)</td>
<td>0.43±0.27 (12)</td>
<td>0.51±0.59 (25)</td>
<td>0.83±0.72 (19)</td>
<td>0.62±0.54 (17)</td>
<td>0.47±0.27 (29)</td>
<td>0.34±0.32 (24)</td>
</tr>
<tr>
<td>Sep</td>
<td>25</td>
<td>34</td>
<td>1.85±0.08 (25)</td>
<td>1.14±0.69 (33)</td>
<td>0.33±0.21 (32)</td>
<td>0.59±0.89 (29)</td>
<td>0.72±0.90 (27)</td>
<td>0.69±0.89 (29)</td>
<td>0.60±0.57 (28)</td>
<td>0.72±0.65 (29)</td>
<td>0.51±0.52 (25)</td>
</tr>
<tr>
<td>Oct</td>
<td>22</td>
<td>32</td>
<td>1.86±0.09 (22)</td>
<td>1.94±0.96 (32)</td>
<td>0.92±1.24 (32)</td>
<td>0.89±1.09 (30)</td>
<td>0.86±1.02 (25)</td>
<td>0.72±0.73 (24)</td>
<td>0.60±0.54 (27)</td>
<td>1.22±0.80 (26)</td>
<td>0.94±1.09 (25)</td>
</tr>
<tr>
<td>Nov</td>
<td>23</td>
<td>38</td>
<td>1.87±0.12 (22)</td>
<td>2.20±1.21 (35)</td>
<td>1.08±1.25 (36)</td>
<td>1.07±1.04 (30)</td>
<td>0.69±0.68 (21)</td>
<td>0.75±0.76 (28)</td>
<td>0.64±0.65 (33)</td>
<td>1.50±1.13 (29)</td>
<td>0.72±0.76 (25)</td>
</tr>
<tr>
<td>Dec</td>
<td>28</td>
<td>34</td>
<td>1.89±0.10 (28)</td>
<td>2.22±1.33 (32)</td>
<td>1.15±1.59 (32)</td>
<td>0.91±0.82 (25)</td>
<td>0.93±0.89 (12)</td>
<td>0.93±0.77 (25)</td>
<td>0.83±0.82 (29)</td>
<td>1.85±0.98 (25)</td>
<td>0.79±0.83 (26)</td>
</tr>
<tr>
<td>Annual</td>
<td>324</td>
<td>379</td>
<td>1.83±0.08 (322)</td>
<td>1.75±0.96 (366)</td>
<td>0.70±0.9 (369)</td>
<td>0.68±0.8 (274)</td>
<td>0.56±0.74 (223)</td>
<td>0.55±0.65 (277)</td>
<td>0.52±0.61 (296)</td>
<td>1.0±0.8 (329)</td>
<td>0.5±0.6 (266)</td>
</tr>
</tbody>
</table>
The levels of these NMHCs decrease towards middle to late spring and are lowest during summer-monsoon, except ethene and propene, which exhibit slightly higher values during summer also. Ethane and propane, which are relatively long-lived species, show pronounced seasonal cycle; however, more reactive species like propene and butane do not show such strong seasonal dependence. The weakest short-term variations are observed in ethane as seen from the 5<sup>th</sup> and 95<sup>th</sup> percentiles, which is due to its longer lifetime, low reactivity and therefore better mixing in the atmosphere.

Propane shows a similar seasonal behavior (figure 5.6c) as observed for ethane. Ethane and ethene show slightly higher values during spring, which could be due to the effects of biomass burning of the northern Indian region. In contrast, ethene and propene show slightly higher levels during summer-monsoon period (particularly during August >500 pptv) and could be associated with the influences from oceanic and biogenic sources [Singh and Zimmerman, 1992]. The higher levels seen in case of propane and butanes during winter could be due to the leakage of unburned liquefied petroleum gas (LPG) during storage, distribution or refilling [Chen et al., 2001; Jobson et al., 2004].
Figure 5.6: Box plot showing the seasonal variations in C$_2$-C$_5$ NMHCs at Nainital during 2009-2011 period. The red and black solid lines inside the box indicate the mean and median values respectively. The whiskers below and above are 10$^{th}$ and 90$^{th}$ percentiles and the 5$^{th}$ and 95$^{th}$ outliers are shown by filled circles.

In tropical Indian region, systematic and long-term measurements of NMHCs have been very limited particularly for remote sites and is only available at Mt. Abu, western India [Sahu and Lal, 2006]. The observed late autumn and early winter type maxima in NMHCs at Nainital may be due to the accumulation of pollutants
because of their longer lifetime and transport time. This also highlights their slower removal from the atmosphere, as the OH concentration in the Northern Hemisphere is at its minimum during winter [Spivakovsky et al., 2000]. Some contribution to this winter maxima could also be associated with the long-range transport of air masses from Africa/Europe [Kumar et al., 2010]. Additionally, a shallower boundary layer during winter [Sarangi et al., 2014] traps them in smaller volume which could increase the mixing ratios. The summer-minimum in NMHCs is mainly due to the arrival of cleaner marine air masses associated with the southwest monsoon. In addition, the NMHCs removal processes are rapid due to maximum OH concentrations. The emissions of C2-C5 hydrocarbons from terrestrial source is suggested to take place during the growing season, whereas the seasonal cycle of oceanic emissions is largely unknown [Laurila and Hakola, 1996].

5.1.2. Seasonal variations in C2-C5 NMHCs at Haldwani and Pantnagar

The observations of light (C2-C5) NMHCs were made at two nearby semi-urban sites (Haldwani and Pantnagar) in the Indo-Gangetic Plain (IGP) region. The seasonal variations in light NMHCs for the two sites are shown in figure 5.7 for the year 2010 and 2011. The seasonal cycle is not much pronounced at the two sites; however, an enhancement during late autumn and winter is seen. Probably, seasonality is not very clear due to availability of less data counts and more scatter due to vicinity to the local sources at Haldwani and Pantnagar as compared to Nainital. Propene values are observed to be slightly higher during summer-monsoon (JJA) while, ethene values are observed to be lower. The emissions of propane, acetylene, and butanes, from urban and industrial sources could be higher due to evaporation...
during the summer. Similarly at Pantnagar, the levels of ethane and ethene are also observed to be higher during wintertime. The observations for summer (JJA) period are not available at Pantnagar.

The annual mean mixing ratios of ethane, ethene, propane, propene, \textit{i}-butane, acetylene, \textit{n}-butane and \textit{i}-pentane at Haldwani are 2±1 ppbv, 1.62±0.99 ppbv, 2.44±1.65 ppbv, 1.66±1.79 ppbv, 2.71±2.05 ppbv, 2.56±1.99 ppbv, 2.78±1.60 ppbv and 4.21±2.16 ppbv respectively. The annual mean mixing ratios of ethane, ethene, propane, propene, \textit{i}-butane, acetylene, \textit{n} butane and \textit{i}-pentane at Pantnagar are 3.73±1.8 ppbv, 2.37±1.79 ppbv, 1.49±1.68 ppbv, 0.82±1.05 ppbv, 1.25±1.61 ppbv, 0.94±0.90 ppbv, 2.75±1.95 ppbv and 1.33±1.85 ppbv respectively.
Figure 5.7: Line plot showing the seasonal variation in C₂-C₅ NMHCs at Haldwani and Pantnagar during 2010 and 2011 respectively. The error bars signify 1-sigma standard deviation.

The number of samples collected at Haldwani and Pantnagar during January to December is given in the Table 5.2. The number of samples at Pantnagar is relatively less in comparison to the number of samples at Haldwani.
**Table 5.2:** The number of samples collected and analyzed during each month at Haldwani (HLD) and Pantnagar (PNT) for the year 2010 and 2011 respectively are shown.

<table>
<thead>
<tr>
<th>Month</th>
<th>No. of Samples Collected at HLD and PNT</th>
<th>Ethane</th>
<th>Ethene</th>
<th>Propane</th>
<th>Propene</th>
<th>i-butane</th>
<th>acetylene</th>
<th>n-butane</th>
<th>i-pentane</th>
</tr>
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<tbody>
<tr>
<td>Jan</td>
<td>--/2</td>
<td>--/2</td>
<td>--/2</td>
<td>--/2</td>
<td>--/1</td>
<td>--/2</td>
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<td>Mar</td>
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<td>Jun</td>
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<td>2/--</td>
<td>1/--</td>
<td>1/--</td>
<td>2/--</td>
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<td>Jul</td>
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<td>Aug</td>
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<tr>
<td>Annual</td>
<td>55/19</td>
<td>54/18</td>
<td>54/17</td>
<td>52/17</td>
<td>47/15</td>
<td>49/13</td>
<td>51/18</td>
<td>49/17</td>
<td>36/16</td>
</tr>
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</table>

In general, the mean levels of NMHCs are nearly similar at Pantnagar and Haldwani. The autumn and early winter maxima at Haldwani and Pantnagar respectively could be due to the local emission of pollutants (e.g. vehicular exhaust, small scale industries etc.). Sometimes the values are also high during spring (MAM), which leads to the photochemical production of ozone at these sites [Ojha et al., 2012]. It is observed that the levels of NMHCs in the Indo-Gangetic Plain sites are as high as about 1.5 times as that at Nainital in the central Himalayas and is nearly similar and within the 1 sigma variability, to an urban site Ahmedabad in western India [Sahu and Lal, 2005].
The measurements of NMHCs are also compared with some of the other
global urban and semi-urban sites such as Foshan in China (December 2008) [Tan et al., 2012]; Heraklion Voutes, Crete, north-eastern Mediterranean (Marc 2006-Feb 2007) [Koulouri et al., 2008; Arsen et al., 2009]; Southern Taiwan (10-13 Oct, 25-
28 Oct 2002) [Chang et al., 2005]; Bombay, India (Mar 1993-May 1994) [Rao et al., 1997]; Beijing, China (Jun-Sep, 2008) [Wang et al., 2010]. The wintertime
measurements of ethane, ethene, propane, propene, acetylene and i-pentane made at
Foshan were higher by ~15 ppbv, ~15-20 ppbv, ~10-12 ppbv, ~5-6 ppbv, ~20 ppbv,
and 8-9 ppbv than Haldwani and Pantnagar, while, the butanes are nearly similar at
these two sites. At Foshan, the higher levels of alkanes were from evaporative
emissions and LPG leakage, whereas higher levels of ethyne (acetylene) had some
contributions from the combustion sources. The major source of i-pentane at Foshan
was gasoline evaporation. The levels NMHCs measured at a European site, island of
Crete, (rural site) were observed to be nearly similar for ethane, ethene and propane,
while the levels of butane and pentane are higher (~2-3 times) at Haldwani, during
winter. This site also exhibits a wintertime maxima, due to the reduced
photochemistry and increased emission particularly from fuel consumption. The
average mixing ratios of NMHCs measured at Kaohsiung, Taiwan were higher by
~2.5-5 ppbv in case of acetylene and ethene whereas the levels of ethane, propane
and propene slightly higher than that at Haldwani and Pantnagar. The value of n-
butane is nearly similar at these sites.

The higher levels of NMHCs observed over Taiwan are due to heavy
industries and traffic. The average mixing ratios of NMHCs (which also included
higher hydrocarbons, other than C2-C5) at PKU site, Beijing, China during Jun-Aug
(21.1 -34.5 ppbv) were higher than that of Haldwani and Pantnagar. The PKU site is
considered to be representative of a typical urban environment in Beijing [Song et al., 2007]. The mean concentrations of ethane, propane, acetylene, i-butane, n-butane and i-pentane at Bombay (measured at 5 different sites) are reported to be 0.5-2.8 ppbv, 1.4-15.4 ppbv, 0.4-1.7 ppbv, 1.8-10 ppbv, 6.1-32.2 ppbv, and 8.3-47.1 ppbv respectively. The higher mean values observed at the Bombay sites, were attributed to the photochemical industries, fugitive emissions due to malfunctioning of some piping and also due to meteorological conditions particularly wind direction.

5.2. Comparison of CH₄ and Light NMHCs With Other Sites

Figure 5.8 shows the comparison of CH₄ seasonal variation observed at Nainital with measurements over other global high altitude sites Mauna Loa (MLO) (19.50°N, 155.6°W, 3400 m asl) in USA (www.esrl.noaa.gov), Jungfraujoch (JFJ), (46.55°N, 7.98°E, 3580 m asl) in Europe [Balzani et al., 2008] and Mt. Abu (24.6°N, 72.7°E, 1680m asl) in western India [Naja et al., 2003b]. The observations at MLO and JFJ are representative of recent times i.e. 2009-2011 and 2005 respectively, while Mt. Abu observations were made during 1993-97 and are shown by an asterisk mark.
Figure 5.8: Bar plot showing the comparison of Methane observations at Nainital (NTL) with Jungfraujoch (JFJ) [Balzani et al., 2008]; Mauna Loa (MLO) [www.esrl.noaa.gov]; and Mt. Abu. [Naja et al., 2003b]. Star symbol in Mt. Abu represents that the data is of the year 1993-97.

The methane values at NTL during winter (DJF) are higher (1.88±0.09 ppmv), while, these are slightly lower at JFJ (1.83±0.01 ppmv) and MLO (1.82±0.005 ppmv). However, springtime (MAM) levels do not show much difference as during spring degradation of these compounds is faster due to higher OH concentrations.

The CH$_4$ values at Mt. Abu show a slightly different seasonal pattern with values of ~1.68±0.03 ppmv during autumn (SON) and ~1.69±0.01 ppmv during spring (MAM). The observations of CH$_4$ were also made over a tropical rural site in southern India, Gadanki (13.5°N, 79.2°E) during 1993-96 [Naja and Lal, 2002]. The annual average concentrations of CH$_4$ at NTL, Mt. Abu and Gadanki are 1.82±0.08 ppmv, 1.63±0.04 ppmv and 1.70±0.11 ppmv respectively.
Figure 5.9: Comparison of seasonal variations of measured NMHC species at Nainital with observations at other mountain and remote sites. The error bars represent standard deviation (one-sigma).

The observed seasonal variation in NMHCs at Nainital has been compared with observations from other remote locations and some sites located in middle and higher Northern Hemispheric latitudes (figure 5.9), where meteorological conditions and degree of photochemical processing could be different from Nainital. The
surface measurements of light NMHCs over mountain sites such as, Mt. Abu (24.6°N, 72.7°E) [Sahu and Lal, 2006], Pallas (67°58’ N, 24°07’ E) [Laurila and Hakola, 1996], and Mauna Loa (19.50° N, 155.6° W) [www.esrl.noaa.gov]; remote sites, e.g. Greenland (72.57° N, 38.48° W) [Swanson et al., 2003] and Harvard Forest (42.54° N, 72.18° W) [Goldstein et al., 1995] and a marine site, Uto (59°47’ N, 21°23’ E) [Laurila and Hakola, 1996], have been used for the comparison. The data for these sites; Mt. Abu, Uto, Pallas, Summit Greenland, Harvard Forest and MLO are for the year 2002, January 1993-December 1994, 1994, June 1997-98, August 1992-July 1994 and 2009-2010 respectively. The data sets are all seasonal studies with various temporal resolutions, which have been converted to monthly average for comparison. For MLO, only ethane, propane, i-butane and n-butane observations were available.

The levels of ethene, i-butane and n-butane are observed to be considerably higher throughout the year at Nainital as compared to other sites. In contrast, ethane variations at Nainital are observed to be within the 1-sigma variations of most of the comparison sites, except Mt. Abu and Mauna Loa. Notably, the levels of ethane, propane, i-butane and n-butane are observed to be lowest throughout the year at Mauna Loa (e.g. ethane = 0.5 ppbv in January) than other sites (ethane = 1.9 to 2.8 ppbv in January). It is also clearly observed that the variability in the observations, as evident from the 1-sigma, is very high at Nainital (0.2-1.2 ppbv in n-butane) as compared with the other sites (0.005-0.6 ppbv in n-butane). The higher variability at Nainital site could be associated with its vicinity to the highly polluted Indo-Gangetic Plain region from where polluted air masses can be transported in favorable meteorological conditions. The annual mean values of ethane are 1522,
1539, 1384, 1786, 1233 and 1759 pptv for Uto, Pallas, Greenlad, Harvard Forest, Mt. Abu and Nainital respectively.

Propene levels at Uto are higher than that over Nainital during late autumn, winter and early spring, whereas the levels during the monsoon period are within the variability. At Uto the higher levels during winter are attributed to the accumulation of volatile organic compounds (VOCs). Due to more efficient convective mixing and synoptic advection of the pollution from nearby source region (IGP), the levels of some of the NMHCs at Nainital are higher. It can be noted here that, the average levels of CO and NO\textsubscript{y} are also shown (Chapter 3) to be higher as compared with other global sites.

5.3. Correlation Analysis

5.3.1. Inter-species Correlation

Inter-species correlations among different NMHCs can provide invaluable information regarding the contribution of different sources at Nainital. The chemical signatures of air masses vary due to different transport times, even if sources are common, implying different levels of photochemical processing. Figure 5.10 (a-d) shows the scatter plots between some important NMHCs (e.g. ethane, propane, acetylene, i-butane and n-butane) measured at Nainital during four seasons; winter (DJF), spring (MAM), summer-monsoon (JJA) and autumn (SON).

The relatively better correlations seen during the autumn/winter indicate a linear accumulation of NMHCs, which changes to slight decay during spring and finally to slow decay or steady state in summer. Few of these inter-species
correlations were also reported from other sites including Harvard Forest [Goldstein et al., 1995, 1996], Izana Global Atmospheric Watch (GAW) station [Schmitt and Thomas, 1997], summit Greenland [Swanson et al., 2003]. The correlations between different hydrocarbons are observed to be poor during summer-monsoon due to dilution with cleaner marine air masses.

Figure 5.10: Correlation between various NMHC species observed during 2009-2011 at Nainital.
In remote locations, the source characterizations for short-lived species (ethene, propene, butanes and i-pentane) are more difficult as compared to relatively long lived species (ethane, propane and acetylene). The major sources of ethane and propane include natural gas leakage and petrochemical industries while fractions of butanes are high in LPG products. Emission ratios of ethane and propane can remain distinguishable for several days from their background values, as the tropospheric lifetime of ethane and propane are longer, and the relationship between ethane and propane has been used in previous studies to provide estimates of the OH concentration and to characterize their emission sources [Wang and Zeng, 2004; Honrath et al., 2008]. The ethane/propane ratio is ~1.5 for fossil fuel combustion [Hough, 1991] while, the ratio varies between 1 and 5 for emissions from biomass burning [Rudolph et al., 1995]. The ratio (slope) and r² values among different hydrocarbons measured at Nainital are given in Table 5.3. The ethane/propane ratio during spring at Nainital is slightly higher than 1 signifying the contribution of northern Indian biomass burning during this time period of the year. During all other seasons the ratio is less than 1 and could be associated with the transport of photochemically aged air mass to the site.
Table 5.3: Correlation coefficient ($r^2$) and the slope values for different set of hydrocarbons at Nainital for the four seasons during 2009-2011 are given.

<table>
<thead>
<tr>
<th>Species</th>
<th>$r^2$</th>
<th>Slope</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>DJF</td>
<td>MAM</td>
</tr>
<tr>
<td>Ethane-Propane</td>
<td>0.15</td>
<td>0.25</td>
</tr>
<tr>
<td>Acetylene-Propane</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Ethene-Propene</td>
<td>0.4</td>
<td>0.08</td>
</tr>
<tr>
<td>i butane-n butane</td>
<td>0.3</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Propane is considered as a tracer of LPG, while acetylene is a tracer of incomplete combustion processes [Russo et al., 2011]. The ratio of propane/acetylene is higher in autumn (SON) and spring (MAM) compared to summer and winter. This suggests a strong influence from LPG, natural gas and evaporative emissions comparative to fossil fuel or combustion related sources [Russo et al., 2011]. The slope values of propene vs. ethene at Nainital (0.15-0.24) are found to be similar to another remote site Jianfeng Mountain (~0.13 ppbv/ppbv) in the south east of China [Tang et al., 2007]. It has been shown in earlier studies that i-butane/n-butane ratio is 0.46 for LPG emissions, and 0.6 to 1 or more for natural gas emissions [e.g. Jobson et al., 1998; Fujita, 2001; Choi and Ehrman, 2004]. The i-butane to n-butane ratio obtained during autumn (SON) at Nainital is 0.5, indicating the influence of mixing of sources like LPG emissions and natural gas.
5.3.2. Acetylene (C₂H₂)-CO Correlation: Photochemical Age of Air Mass

The variations in hydrocarbons can be useful indicators of the age of an air mass, effectively when they have similar sources but different lifetimes [e.g. Parrish et al., 1992]. The mixing ratios of both C₂H₂ and CO have nearly similar atmospheric cycles, as they have common sources associated with combustion processes and are generally removed by reactions with OH.

Figure 5.11 (a-d) shows the scatter plots between C₂H₂ and CO for four different seasons. The correlation is positive in all the seasons indicating their transport from common sources. The scatter in the data is generally due to the remoteness of the site from these sources. Since, Acetylene has a much shorter lifetime (2 weeks) as compared with CO (2 months), thus as an air mass ages, the C₂H₂ mixing ratio decreases faster, lowering the C₂H₂/CO ratio. C₂H₂/CO ratios less than 0.5 are shown to be the representative of well-aged air masses, while, the ratios greater than 1.0 are associated with relatively fresh emissions (only few days old) [Gregory et al., 1996].
Figure 5.11: Scatter plot between CO and Acetylene ($C_2H_2$) is shown for four different seasons (a) winter (DJF), (b) spring (MAM), (c) summer-monsoon (JJA) and (d) autumn (SON) at Nainital.

The $C_2H_2$/CO ratio (slope) for winter (DJF), spring (MAM), summer-monsoon (JJA) and autumn (SON) are estimated to be ~0.5, 0.95, 0.06 and 1.68 respectively. The ratio obtained for winter shows that air masses reaching Nainital is not very old and can be considered as moderately aged air mass, while during summer, the ratio is much less than 0.5, when pristine air mass arrive to the site and the air mass is well aged. On the contrary, during spring and autumn, $C_2H_2$/CO ratio is greater than 0.5, which shows that during these seasons the site is under the influences of fresh
emissions. This is mainly because of the transport of IGP pollution due to stronger convection and air mass circulation over IGP region. This analysis of C$_2$H$_2$/CO ratio is also in agreement with our results based on CO and NO$_y$ observations at Nainital [Sarangi et al., 2014].

5.3.3. Temperature Dependence of Acetylene

In Figure 5.12, the seasonal variation in acetylene is shown along with the surface temperature. It is observed that acetylene is in general in a negative relationship with the ambient temperature. Acetylene mixing ratios are observed to be highest during winter (0.99±1.2 ppbv in January) when the ambient temperature is lowest (~9±2.5 °C in December). This anti-phase relationship is attributed partially to the changes in meteorological conditions and to the chemical removal of acetylene in high temperature conditions. During the summer-monsoon, the photochemical lifetimes are also at their minimum. Such feature was also seen at Fraserdale (50° N), Ontario, Canada [Jobson et al., 1994] in mid-latitude region.

![Figure 5.12: Seasonal variation in acetylene and surface temperature at Nainital.](image-url)
5.3.4. Influence of Photochemical Processing

In order to understand the factors contributing to the seasonal variations of NMHCs at Nainital and to determine the photochemical age of an air mass and the dominance of OH oxidation [Jobson et al., 1994; Bottenheim and Shepherd, 1995], an analysis using hydrocarbon ratios has been conducted [Rudolph and Johnen, 1990; Parrish et al., 1992; McKeen et al., 1996]. Figure 5.13 (a) shows the correlations for hydrocarbons ratios of ln([n-butane]/[ethane]) versus ln([i-butane]/[ethane]), which have similar lifetimes. Correlations between NMHCs with similar OH rate constants minimizes the effect of dilution [Jobson et al., 1994], thus if the dilution effects are neglected, then the relation of hydrocarbons (alkanes) can be expressed as

\[
\ln\left(\frac{\text{i-butane}}{\text{ethane}}\right) = M^* \ln\left(\frac{\text{n-butane}}{\text{ethane}}\right) + C \quad (1)
\]

Details and derivation of this relation is reported in Swanson et al., [2003]. The slope of equation (1) is given by

\[
\frac{(K_{\text{i-butane}} - K_{\text{ethane}})}{(K_{\text{n-butane}} - K_{\text{ethane}})}
\]

(2)

Where, C is the intercept of linear relation and Ks are reaction rate constants due to OH reactivity. Figure 5.13(a) shows the correlation for two contrasting seasons winter (DJF) and summer (JJA), as these two seasons represent seasonal maxima and minima at Nainital respectively. This gives slope values of 1.1 and 0.97 for winter and summer respectively. These results are in good agreement with Jobson et al., [1994], Swanson et al., [2003], who reported slope values of 0.97, 0.93
respectively for measurements at remote sites. While the winter season slope value at Nainital is slightly greater than the reported slopes.

![Graph showing natural logarithm plots of hydrocarbons](image)

**Figure 5.13**: (a) The natural logarithm plot of hydrocarbons; ln([n-butane]/[ethane]) with ln([i-butane]/[ethane]) is shown during winter and summer.
season along with the slope values of each season, (b) A plot of [i-butane] vs [n-butane] (black circles) with indicated slope value for the period of January 2009-December 2011. The red circles are plot of [i-butane]/[n-butane] versus [n-butane] to check for analytical bias at low concentrations.

It has been suggested that [McKeen et al., 1996], slope values of about 0.92 indicate the decrease of NMHCs mainly by oxidation, while, slope value will be much lower if mixing with the background air dominates. Figure 5.13 (b) shows the plot of i-butane concentration against the n-butane concentration. As i-butane and n-butane have similar sources and photochemical lifetimes, thus the concentration ratio of i-butane to n-butane throughout the year should be nearly similar. The slope of this plot is 0.37 (r = 0.50), with highest concentrations observed in winter and lowest in summer. This slope value is similar to the slope value of 0.47 (r = 0.985) reported over Fraserdale, Canada (50° N) [Jobson et al., 1994]. Figure 5.13(b) also shows i-butane/n-butane ratio as a function of n-butane. During summer-monsoon, these species are in the 100-1000 pptv range. The plot shows significant scatter and poor correlation coefficient. Even at low concentrations, no skew is evident and the ratio is centered on ~0.5, giving some measures of confidence in the precision of the measurements, which also agrees with the results of Jobson et al., [1994].
5.3.5. Correlation of CO with Ethane and Propane

Ethane and propane are the most common anthropogenic hydrocarbons; their variations are associated with the emissions from primary sources with subsequent atmospheric oxidation and dilution. However, carbon monoxide (CO) sources in the atmosphere include fossil fuel combustion, biomass burning and oxidation of methane and other hydrocarbons [Jaffe et al., 1997]. CO, ethane and propane have atmospheric lifetimes longer than 10 days [Greenberg et al., 1992]. CO was compared with ethane and propane for upslope condition during four different seasons (Figure 5.14). During winter, spring and autumn seasons, the concentration of CO shows a good positive correlation while during summer-monsoon period the correlation is relatively poor (Table 5.4).
Figure 5.14: The scatter plots of ethane, propane with CO for the upslope flow period, along with a linear regression fit for four different seasons during 2009-2011 at Nainital.

In all the seasons, correlations of ethane with CO are better than that with propane. The slopes of the linear regression differ significantly with season and higher NMHC/CO ratios are observed during winter. Lowest slope values are observed during summer and spring, due to faster loss of propane compared to CO, while, ethane is destroyed at approximately the same rate as of CO. The seasonal differences may also represent varying source ratios. The correlation coefficients are
higher during autumn and winter period, while, these are lowest during summer owing to transport of marine air mass. Such variations in slopes were also observed over the Mauna Loa observatory (MLO) [Greenberg et al., 1996] between ethane, propane and CO during winter (higher slope) and summer (lower slope).

Table 5.4: correlation coefficients (r^2) and slope values at Nainital of each scatter plot for the four seasons during the year 2009-2011 is given.

<table>
<thead>
<tr>
<th>Site</th>
<th>Winter (DJF)</th>
<th>Spring (MAM)</th>
<th>Summer (JJA)</th>
<th>Autumn (SON)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane/CO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NTL</td>
<td>5.8 (0.53)</td>
<td>4.0 (0.42)</td>
<td>3.1 (0.3)</td>
<td>5.6 (0.5)</td>
</tr>
<tr>
<td>MLO</td>
<td>9.3 (0.91)</td>
<td>8.5 (0.63)</td>
<td>7.9 (0.7)</td>
<td>(0)</td>
</tr>
<tr>
<td>Propane/CO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NTL</td>
<td>2 (0.2)</td>
<td>1.2 (0.14)</td>
<td>-0.06 (0.0002)</td>
<td>4.9 (0.4)</td>
</tr>
<tr>
<td>MLO</td>
<td>3.1 (0.65)</td>
<td>1.5 (0.41)</td>
<td>(0.13)</td>
<td>(0.04)</td>
</tr>
</tbody>
</table>

The slope values at MLO are greater than Nainital during all the seasons of upslope period by a factor of 3.5, 4.5, 4.8 and 1.1, 0.3 during winter, spring, summer for ethane and propane respectively. The ratios are always greater in case of ethane and CO and lower in case of propane-CO at MLO, as seen at Nainital. This suggests that the air arriving at Nainital during summer-monsoon is well aged and did not carry fresh source inputs of NMHCs (except some oceanic source NMHCs like ethene and propene). This also suggests that the influence of atmospheric dilution processes on NMHC concentration is weakest during spring season.
5.4. Summary and Conclusions

Three years of maiden measurements of CH$_4$ and C$_2$-C$_5$ light NMHCs have been presented, during April 2009-December 2011 at Nainital, a high altitude site located in the central Himalayas. The time series of CH$_4$ and NMHCs observations are investigated for day to day and seasonal variations. Seasonal cycle of methane and NMHCs at Nainital is characterized by late autumn and early winter maxima and summer-monsoon minima. The annual mean mixing ratios of methane, ethane, ethene, propane, propene, i-butane, acetylene, n-butane and i-pentane are 1.89±0.09, 1.75±0.96, 0.7±0.9, 0.59±0.76, 0.56±0.74, 0.55±0.65, 0.52±0.61, 1.0±0.84 and 0.49±0.62 ppbv respectively. The seasonal variations in light NMHCs are also presented for two semi-urban sites Haldwani and Pantnagar for the year 2010 and 2011 respectively. Distinct seasonal cycles are not observed at these two sites, which could be due to less number of data points and more scatter in the data due to vicinity to the sources.

A comparison of CH$_4$ levels at Nainital with other global high altitude sites like Jungfraujoch (JFJ) and Mauna Loa (MLO) shows similar variability with winter-high and summer-low at all the three sites. The levels and variability over Mt. Abu is different. The annual mean levels of NMHCs have also been compared with other global high altitude and remote sites. The annual mean values of long lived species like ethane, propane and acetylene are found to be nearly similar with other global sites, except at Mauna Loa. In short lived species such as ethene, propene and butanes, the variability is nearly similar compared to other sites but the levels are slightly higher at Nainital with more variability. The interspecies correlations of NMHCs are observed to be good during autumn/winter and poor
during summer-monsoon. The ratio or the slope values between different NMHCs are used to identify the sources of pollutants. The $\text{C}_2\text{H}_2/\text{CO}$ ratio observed at Nainital during different seasons indicate that the site is under the influence of moderately fresh emissions during spring and autumn, while, it receives well aged air mass during winter and summer, which is consistent with our studies for CO and NO$_x$.

The log-log plot analysis between ln([n-butane]/[ethane]) and ln([i-butane]/[ethane]) was conducted for two contrasting seasons winter (DJF) and summer (JJA). The slope values of these plots were estimated to be 1.1 and 0.97 for winter and summer respectively. These results are in agreement with Jobson et al., [1994] and Swanson et al., [2003]. Correlation analysis further shows better correlations of CO with ethane as compared with propane. Higher NMHC/CO ratios are observed during winter and lowest slope values are observed during summer and spring, as propane is destroyed faster in spring and summer seasons relative to CO, while ethane is destroyed at nearly similar rate of CO. The seasonal differences may also represent varying source ratios.