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Research Article

Temporal Variation of Non-Methane Hydrocarbons in the Ambient Atmosphere of Tezpur Region of Assam

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Abstract: The non-methane hydrocarbons (NMHC) in the atmosphere are important pollutants to study as they are precursors to several secondary pollutants including ozone. This study addressed the temporal variation of NMHC over Tezpur region of Assam. Continuous data of NMHC retrieved by GC-FID based analyzer for the year 2014 were analysed and have been reported in this study. The highest monthly mean NMHC concentrations of 355.0±128 ppb was found in the month of November. In addition to the source strength, atmospheric reactivity and dispersion played a crucial role in the concentration of NMHC in Tezpur region. While the lowest monthly mean NMHC concentration of 73.6±45 ppb was found in the month of February. The monthly polar plots showed that the sources affecting the NMHC concentration in Tezpur region were mostly local; but there was also long-range transport to the area in the month of March and April. The lowest weekly concentration of NMHC was observed on weekends due to lower anthropogenic activities like vehicular movement. The mean concentration of NMHC on Sunday is 143.6±88 ppb. The lowest diel concentrations of NMHC were observed during the afternoon 14:00 and 15:00 hours which were indicative of enhanced reactivity in the atmosphere and high atmospheric dispersion, and the peak NMHC concentration was observed during evening hours.

Keywords: NMHC; Temporal variations; Anthropogenic contribution; Reactivities

1. Introduction

The non-methane hydrocarbons (NMHC) are atmospheric gases that are found in significant amounts over urban, rural as well as remote environments. They are extremely reactive and play a crucial part in the photochemical processes [1-3], and towards maintaining the oxidative behaviour of the atmosphere. They have a high propensity to be oxidized by the hydroxyl (•OH) radical and ozone (O3) found in the atmosphere. More so, the climate is indirectly influenced by the increased air oxidation capacity caused by these photochemical oxidation processes. The NMHCs directly affect radiative forcing as modest greenhouse gases [4],[5]. The reactions of oxides of nitrogen (NOx) with the NMHCs in the presence of sunlight to produce O3 and other oxidants have been well understood and reported [6-12]. It is evident that ground level O3 has impacts on the well-being of human, climate, and ambient air quality [13].

Additionally, the NMHCs aid in the production of secondary pollutants like secondary organic aerosols (SOAs) [11-16] and particulate matter (PM). It was reported that poor ambient air quality has contributed to premature deaths of 4.2 million people worldwide, mainly from exposure to O3 and PM [17]. Besides, NMHCs have the potential to directly degrade air quality, which will have a negative impact on human health [18-20]; and many of them are recognized to have toxic and carcinogenic effects [21]. Benzene, 1,3-butadiene, some polycyclic aromatic hydrocarbons (PAHs) and other polycyclic organic matter (POM), are considered highly carcinogenic and mutagenic NMHCs [19] [22-24].

The NMHCs are emitted from natural and anthropogenic sources [2]. The plants primarily emit isoprene, monoterpenes, and sesquiterpenes [25,26]. Marine emissions and microbial synthesis are other biogenic sources of NMHCs [27]. The major anthropogenic sources of NMHCs comprise motor vehicle exhausts, petrochemical enterprises and natural or LPG gas leaks, biomass burning. The NMHCs with varying degrees of toxicity can be found in landfill gases [28-31]. Globally, anthropogenic sources, including vehicle emissions, industries, refinery operations and fugitive solvent evaporation [32-36] and domestic items such paints, adhesives, coatings, and varnishes dominate the emissions in urban areas. However, in India as well as other South Asian countries, human activities like burning of trash and crop residue have developed as poorly regulated emission sources [37].

The NMHCs make an important group of atmospheric gases for scientific inquiry yet no reported works are found from the region of India represented in the study. Some studies have been reported from the mainland India that focussed on the source identification [38-40], emissions strengths [41-45] and temporal variations [46,47,12,48]. However, a significant void remains in the research on NMHCs from the north-east region of India. The present study is the first attempt to appreciate temporal (diel, weekly, and monthly) variations of ground level NMHC over Tezpur region of Assam for a one-year cycle, and also to understand the sources associated with the variability of NMHC in in the region.

2. Materials and Methods

2.1. Study Site

The monitoring station under the MAPAN (Monitoring of Atmospheric Pollution And Networking) program for measurement of NMHCs and meteorological parameters is located on the Department of Environmental Science, Tezpur University (26.7003° N, 92.8308°E). Tezpur University is situated in a rural area of Tezpur, in Sonitpur district of Assam, where traditional biomass burning like wood, bamboo, crop residue and cow dung is ubiquitous in homes [49]. Additionally, the region is comprised of tea estates having their own processing units, brick kilns, and small-scale industries. The National Highway is at a distance of 7 km from the station. As the crow flies to the north, the foothills of the eastern Himalayas appear about 35 km from the station. The region generally experiences prevailing easterly winds, with seasonal variability influenced by regional south-western monsoon. South-western monsoonal rainfall affects the agriculture, tea plantation and vegetation of the region.

2.2. Data Acquisition

Continuous data of NMHC were measured for the year 2014 using synspec alpha 115 analyser (Ecotech), which work through GC-FID technology with a detection limit of 50 ppb and the range is >100 ppm (100000ppb) [50]. Meteorological parameters—wind speed and wind direction—were measured using Met One Instruments meteorological sensors. The data acquisition system installed in the monitoring station averaged the continuous measurements of NMHC and meteorological parameters to generate hourly mean values, which were used for the present analysis.

2.3. Data Analyses

Descriptive statistics and hypothesis testing were carried out by statistical software R, using base package. The monthly, weekly, and diel variations of NMHC concentrations were analyzed and visualized using the ggplot2 [51,52] package, while monthly polar plots were computed using openair [53] package all within the R statistical environment.

3. Results and Discussion

3.1. Concentrations

The hourly concentration data of NMHC for the year 2014 was taken to calculate mean annual concentration, which is compared with other studies in the same year in India. The annual mean NMHC concentration in the study area was 148.5±103.3 ppb in 2014. A comparative account of NMHC of the present study with other studies has been given in Table 1. According to Nishanth et al. [42], the yearly mean NMHCs was 19.2 ± 5.6 ppb in a rural area along the coasts in Kannur, India. Kotnala et al. [45] found in their investigation that annual average NMHC was 670.0±210.0 ppb in Delhi, India. Majumdar and Gavane [46] found year-round average NMHC concentration of 2020.0 ppb. There was a great variation in the atmospheric NMHC concentrations that have been recorded by different researchers. While the concentration recorded by Nishanth et al. [42] was lower than the present study, concentration recorded by Kotnala et al. [45] and Majumdar and Gavane [46] was may be omitted on the higher side. The study area of Kotnala et al. [45] was in the Delhi metropolitan city and Majumdar and Gavane [46] was the heart of Nagpur city and the other two studies reported NMHC concentration from rural areas. Delhi and Nagpur are large cities with strong source strengths which could be the reason of the high concentrations reported by Kotnala et al. [45] and Majumdar and Gavane [46].

In Tezpur region, the highest monthly mean NMHC concentration was found in the month of November, 355.0±127.9 ppb. While lowest monthly mean NMHC concentration was found in the month of February, 73.6±44.7 ppb. The monthly descriptive statistics of NMHC is given in Table 2. To check the significance of monthly variations, one-way ANOVA is conducted and results shows highly significant with $p < 0.001$ and F value much greater than F critical. Monthly variation is discussed in detail in the later section.

The weekly descriptive statistics are given in Table 3, where mean NMHC concentrations were calculated for each day of the week in the year 2014. The highest NMHC concentration was 154.6±118.2 ppb found on Friday and lowest NMHC concentration was 143.6±88.3 ppb found on Sunday in the Tezpur region. To check the significance of weekly variation one-way ANOVA was conducted. The results indicated that weekly variation is significant as p value = 0.03 and F value was greater than F critical.

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation as well as the experimental conclusions that can be drawn.

3.2. Monthly Variation

The monthly variation of hydrocarbons was mostly influenced by the source strengths, differences in vertical mixing, air mass climatology as well as atmospheric behavior such as increased convection [54,55]. The Fig 1 shows that in the month of November and September concentrations of NMHC were high and in the months of February and July concentrations were low. Because the emission strengths are very different in all these months the variations can be explained by the reactivity of NMHC through atmospheric oxidation. In Tezpur region of Assam cloud cover plays an important role in the elimination of NMHC through oxidation because all the reactions involved are photochemical processes. Literature suggest that the overcast sky in monsoon is a common phenomenon [56] in Assam. According to Nishanth et al. [42] NMHCs during monsoon season is affected by the substantial reduction in solar intensity and hence the reduced photochemical reactions. Low elimination rate might enhance the concentrations in September. Moreover, contributions from biogenic emissions could be profound in the study area during the months when south-western monsoon affected the region due to lush growth in vegetation, as the surrounding areas were covered with paddy fields, tea plantation, and forests. Alternately, NMHC concentrations in the month of July may be attributed to low source strength, high reactivity due to high humidity leading to higher OH radical and short-term decreases in concentration by wet scavenging associated with precipitation events [42].

One of the main sources of NMHC in Tezpur region is extensive household biomass burning. Earlier reports from the study area mentioned increased incidences of biomass burning in the colder months [57]. It is well established that residential cooking [43] and other biomass burning practices are a major cause of NMHC emissions [40,58] in India. The area contains important highways connecting inter and intra state so vehicular emission is also an important contributor to NMHC concentration. There are a huge number of brick kilns in mid-BV and their production starts after rainy season is over. Coal is the major fuel in brick kilns [59]. Additionally, wood and agricultural residues are also used. Coal burning releases fine particulate and gaseous pollutants including NMHCs [60]. The most common NMHCs that are released from brick kilns are benzene, toluene, ethylbenzene and xylenes [61]. NMHC emissions in the study area could also arise from microbial decomposition processes in straw-amended agricultural soils, which are prevalent due to the region’s dominant agricultural practices [62]. These may be the reason of highest mean monthly concentration of NMHC in the month of November.

Another factor which affects the monthly variation of NMHC in Tezpur region is dispersion of NMHC. To understand the relationship of NMHC with wind speed and wind direction the monthly polar plots were computed as shown in Fig 2. The month of November showing the highest mean NMHC concentration (in the colour range red), which was associated with low wind speed in NE and NW directions as well as medium wind speed in SE and SW directions. This indicates in this month there were various local sources affecting the NMHC concentration and also transport of NMHC. In the months of August, September, October and December mean NMHC concentration was high (in the colour range yellow), associated with low to medium wind speed. However, in the month of March and April although the mean NMHC concentration was low (in colour range blue), they were associated with high wind speed which indicates long-range transport of NMHC to Tezpur region. According to earlier reports, air mass trajectories that arrived at the study site originated and/or passed over the **Indo-Gangetic Plain** (IGP) and bring loads of pollutants to the area [63,64,65,66].

3.3. Weekly Variation

Mean NMHC concentrations on the days of the week are shown in Fig. 3 (A). The plot shows that the mean NMHC concentration gradually decreased from Monday to Wednesday then increased and attained maximum on Friday and then decreased on Saturday. NMHC decreased to the lowest concentration on Sunday. The lowest NMHC concentrations in the weekend explained the "weekend effect" on the concentrations of NMHC in Tezpur region. In a VOC-limited regime, lower NOx emissions result in greater reactivity of NMHC [67,68,69]. Because the reactions of NMHC are triggered by the •OH radical, and a significant reduction in NOx makes more •OH radical accessible to start the oxidation of NMHC [70,71]. This could possibly have resulted in the increased degradation of NMHC leading to decreased NMHC concentration on Sunday due to reduced vehicular activity on weekends as combustions of fossil fuel is one of the main sources of NOx. The Fig. 3 (B) shows the variation of mean NMHC concentration as days progressed in a week, which clearly showed the shortest diel peak on Sunday. Detailed diel variation of NMHC concentrations are discussed in the next section.

Majumdar and Gavane [46] mentioned that there was a mild weekend effect in NMHC emission in Nagpur city that most likely highlighted to a slight positive impact of a larger fleet of on-road vehicles and increased weekday commercial activity on ground-level NMHCs. Traffic-driven NMHC emissions have been discussed in previous studies [72,73], which found NMHC concentrations related to traffic movement.

3.4. Diel Variation

The variations of mean hourly concentrations of NMHC, are shown in Fig. 4. The concentration gradually decreased from the mid-night and attained the lowest concentration in the afternoon at 14:00 and 15:00 hours. As sunlight continues to heat the earth's surface in the morning, the temperature inversion eventually breaks, allowing lesser-polluted free tropospheric air to dilute these gases to their lowest levels in the afternoon [12]. Due to the photochemical oxidation of NMHC in the atmosphere as well as the influence of meteorological factors like solar radiation, temperature, wind speed, the lowest concentration of NMHC was observed in the afternoon hours. After attending the lowest concentration in the afternoon, a steep increase in NMHC concentration was observed and a peak was formed in the late evening at 19:00 hour due to the accumulation and formation of an inversion layer at a very low height [70]. In the evening traffic is high, which contribute towards the emission of ethene, acetylene and propene. These NMHCs are mainly emitted from vehicles due to incomplete combustion of fossil fuels [74]. Being the most abundant and having low reactivity, ethane and propane [12], accumulate in the atmosphere in the evening.

The NMHC concentration decreases before mid-night as the nighttime chemistry of gas-phase alkene ozonolysis [2] takes place. In daytime the •OH radicals oxidize volatile organic compounds (VOCs) to produce oxidizing radicals such alkyl radicals, alkoxy radicals and peroxy radicals. These oxidants take part in the reaction to photolyse NO to NO2 [2,75,76]. Although ozonolysis, the O3 addition mechanism, is much slower in daytime, it becomes more significant at night when photochemically produced OH radicals are lower [2]. Additionally, anthropogenic emission of NMHC decreases at night which leads to lower concentration. It was interesting to see that there was a small peak in the early morning at 07:00 hour due to due to the breakdown of the nocturnal inversion layer. However, the peak formed in the evening is more prominent. In general, emission strength, oxidative capacity, meteorology, and planetary boundary layer height (PBLH) are the reasons for the diel variation of NMHC in the Tezpur region.

Similar results in the diel variations were also reported from elsewhere. In a study by Sahu et al. [12] reported ethane, propane, i-butane, and n-butane concentrations to have peaked in the early morning. Pentane (i-C5H12 and n-C5H12) showed a single peak between 18:00 – 00:00 hr. Osaka city [77] which showed greater prominence in the morning hour peak compared to the evening hour peaks. Another study by Nishanth et al. [42] at a rural site in Kannur found that NMHC exhibited a build-up in the early morning; a very low concentration was noted at midday, and thereafter an increase in concentration during the evening hours. As per their studies, the main factor affecting NMHC distributions was the source strength. Majumdar and Gavane [46] reported from Nagpur, India that concentrations at 8:00 hour and 23:00 hour were typically lower than at 13:00 and 18:00 hour in all seasons. They attributed the increased concentrations in Nagpur during 13:00 and 18:00 hour to traffic and business activity.

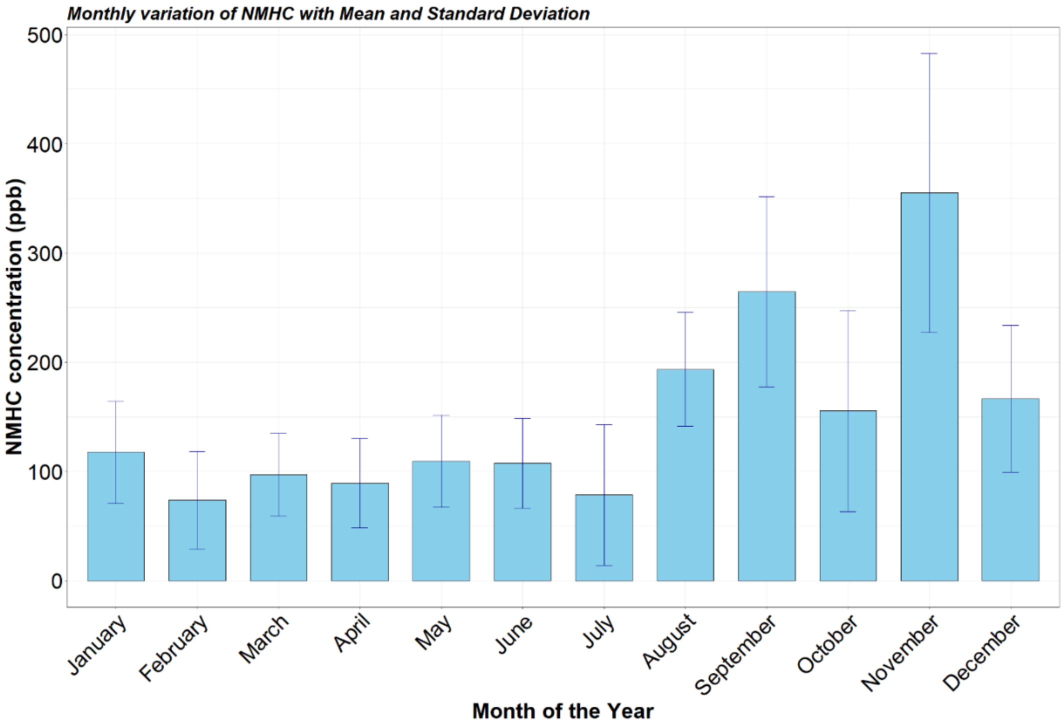

Figure 1. Monthly variation of NMHC concentrations through a yearly cycle in the ambient air of Tezpur

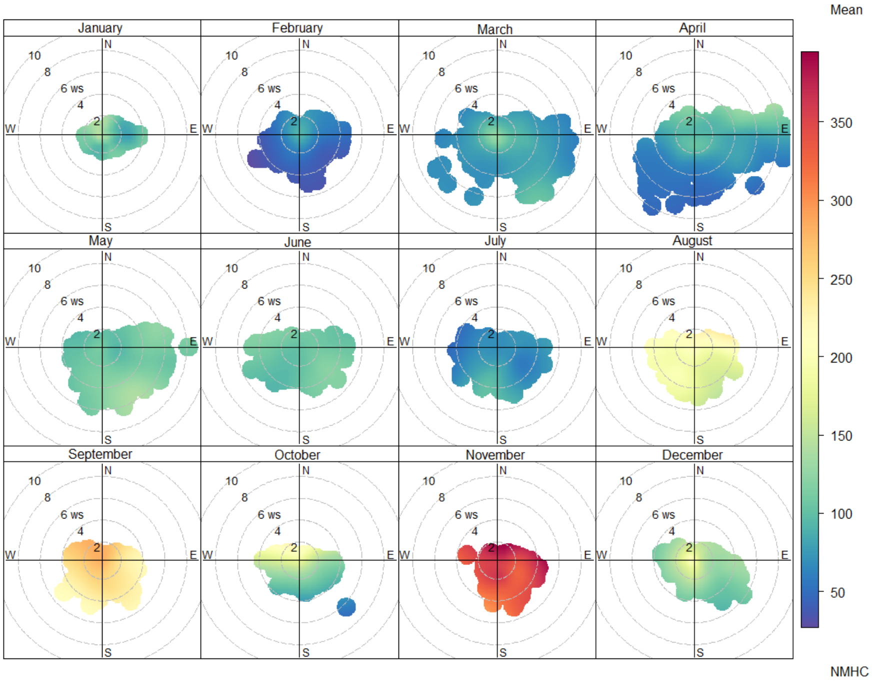

Figure 2. Polar plots of monthly NMHC concentrations in the ambient air of Tezpur

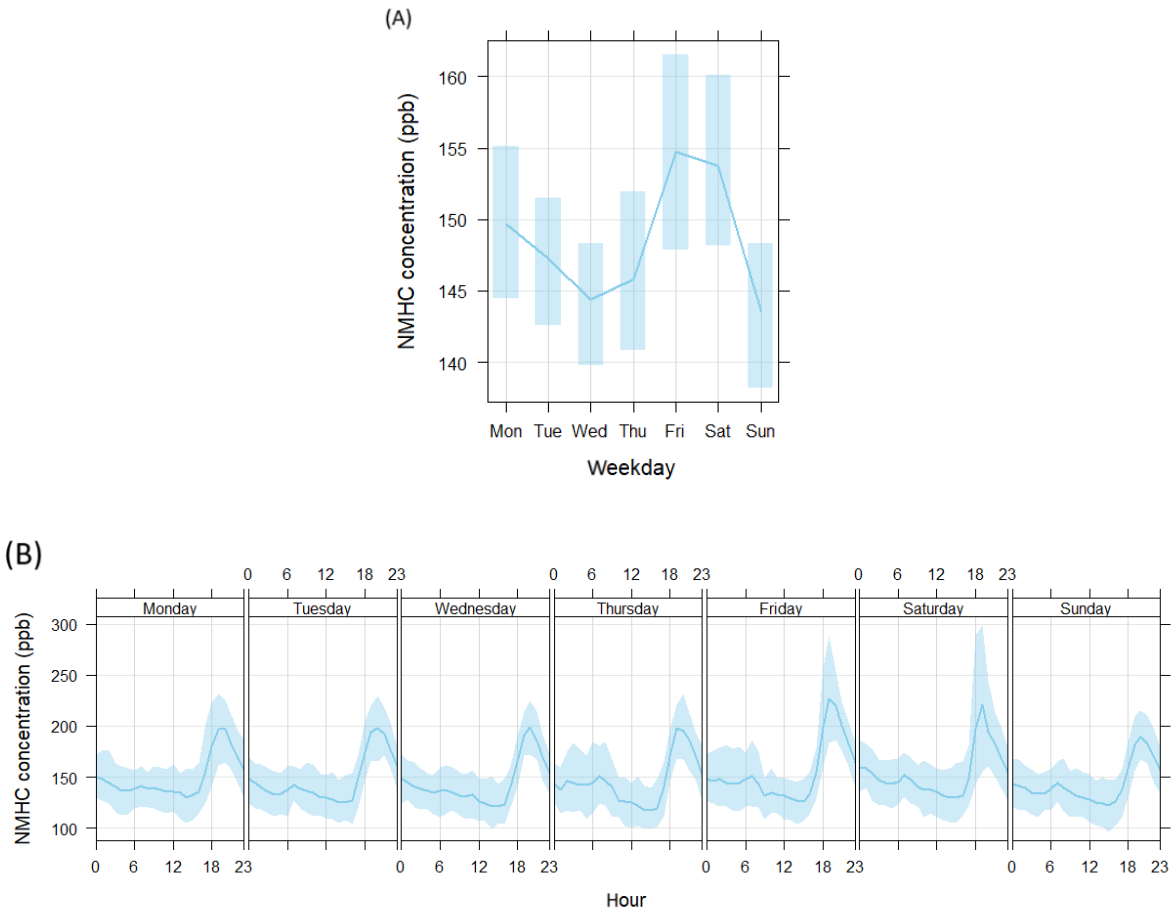

Figure 3. (A) Weekly variation of NMHC concentration and, (B) Variation of NMHC concentration as day progressed in a week in the ambient air of Tezpur

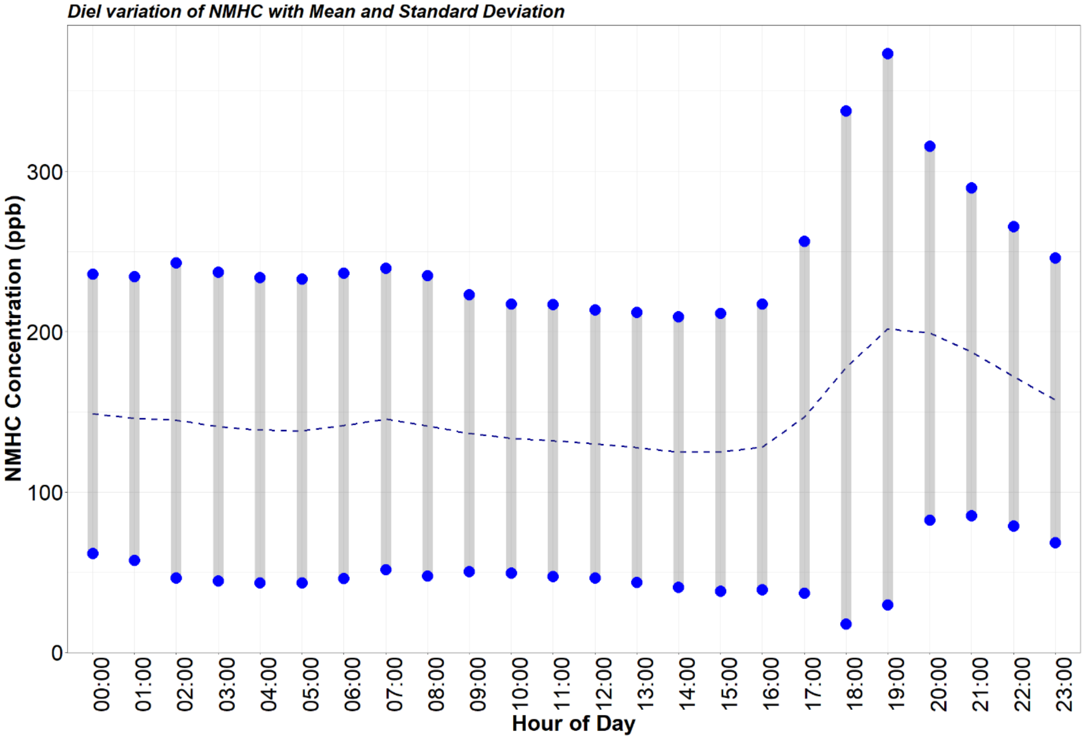

Figure 4. Diel variation of NMHC concentration in the ambient air of Tezpur

Table 1. A comparative account of concentration of NMHC in the ambient air of Tezpur with concentration elsewhere in India

Sl.	Region/study	Land use	Mean (ppb)	SD (±ppb)	Major sources	References
1	Mid-Brahmaputra valley, India (2014)	Rural	148.5	103.3	Biomass burning, coal burning, vehicular emission, biogenic emissions	Present study
2	Kannur, India (2009 – 2011)	Rural	19.2	5.6	Biomass burning, biogenic emission, emission from fertilizers	[42]
3	Delhi, India (2014)	Urban	670.0	210.0	Vehicular emission	[45]
4	Nagpur, India (2013 – 2014)	Urban	2020.0	-	Vehicular emission, LPG emission	[46]

SD, standard deviation, "–" indicates that SD values are not available in the literature

Table 2. Descriptive statistics of monthly concentration of NMHC in the ambient air of Tezpur

Month	Mean (ppb)	SD (±ppb)	F value	F critical	p value
January	117.7	46.8	1101	1.789758	0.0000
February	73.6	44.7			
March	97.0	37.8			
April	89.1	40.9			

Contd.

Table 2. Descriptive statistics of monthly concentration of NMHC in the ambient air of Tezpur

Month	Mean (ppb)	SD (±ppb)	F value	F critical	p value
May	109.2	42.2			
June	107.5	41.0			
July	78.4	64.6			
August	193.5	52.2			
September	264.5	87.0			
October	155.4	92.1			
November	355.0	127.9			
December	166.6	67.4			

SD, standard deviation

Table 3. Descriptive statistics of weekly concentration of NMHC in the ambient air of Tezpur

Day	Mean (ppb)	SD (±ppb)	F value	F critical	p value
Monday	149.7	97.6	2.266	2.099644	0.0346
Tuesday	147.2	92.7			
Wednesday	144.4	89.3			
Thursday	145.8	104.7			
Friday	154.8	118.2			
Saturday	153.7	125.7			
Sunday	143.6	88.3			

SD, standard deviation

4. Conclusions

The concentration of NMHC varied considerably in Tezpur region of Assam during the period of study. NMHC concentrations showed explicit monthly, weekly and diel variations, which is inherent with the atmospheric NMHCs. NMHC concentrations were lowest in February and highest in November, which is supported by monthly calculated polar plots. These observations suggests the combined influence of local emission strength, meteorological conditions, and chemical transformation processes on monthly variation of NMHC concentrations. Polar plots for March and April months showed high probability driven by meteorological conditions characterized by strong air mass movement indicating long range transport. Weekly variation showed reduced concentrations on weekends, reflecting lower anthropogenic emissions. The study highlights distinct diel patterns in NMHC concentrations, with peak observed during evening hours and the lowest concentrations in the afternoon, likely influenced by boundary layer dynamics and photochemical activity.

Multidisciplinary Domains

This research covers the domains: (a) Measurement of organic gases by GC-FID technique (b) Statistical analysis and data visualization (c) Meteorological dependency of NMHC (d) Chemistry of the atmosphere (e) Anthropogenic activities affecting the atmospheric composition and processes.

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Conflicts of Interest

The authors declare no conflict of interest.

Declaration on AI Usage

This manuscript has been prepared without the use of AI tools.

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