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Study of C₂–C₅ Non-methane Hydrocarbons and Their Ozone Formation Potential at Bhubaneswar, an Eastern Coastal Site in India

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Abstract: A preliminary study has been taken up to evaluate the NHHCs concentration and their effect on atmospheric chemistry at Bhubaneswar for the very first time during winter months when pollution load is prevalent. For this purpose ambient air samples were collected during a period of 3 months (Dec 2013–Feb 2014). The samples were analyzed for C_2–C_5 light non-methane hydrocarbons (NMHCs) using a gas chromatograph with a thermal desorption system. It was observed that level of NMHCs over the measurement site was lower in comparison to other urban locations within India but higher in comparison to Bay of Bengal. Statistical interpretation suggests a non-significant variation of NMHCs concentration between the observation months. Diurnal observations revealed a higher concentration of both *n*-pentane and *i*-pentane which was mostly attributed to solvent evaporation. Liquefied petroleum gas usage is believed to be a major contributor to the mixing ratios of propane (1.5 ppbv) and butane (0.027 ppbv) while ethane and ethylene emissions were attributed to traffic volume and vehicular exhausts. The propylene-equivalent and ozone formation potential of NMHCs have also been calculated in order to find out their OH reactivity and contribution to the photochemical ozone formation. Relative humidity was also observed to have a significant correlation with NMHCs concentration. Variation of total non-methane hydrocarbons (TNMHCs) with ozone and CO suggest the role of TNMHC as precursor for ozone formation.

1. Introduction

A steady increase in atmospheric pollutants has been observed over different places within the Indian subcontinent pertaining to globalization and economic development [1, 2]. Growth and expansion in various developmental sectors i.e. industry, automobile, infrastructure, agriculture etc. have lead to manifold increase in emission levels of various air borne pollutants e.g. carbon monoxide (CO), nitrogen oxides (NO_x), oxides of sulfur (SO_x) and other volatile organic carbons (VOCs). Amongst other VOCs, light NMHCs play an important role in tropospheric chemistry as precursors of surface ozone (OZONE) in presence of hydroxyl (OH) radical along with the oxides of nitrogen(NO_x) or CO [3, 4] as given by the following reactions from Eqs. (1–8) [5, 6].
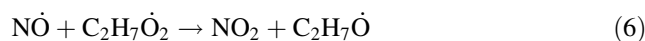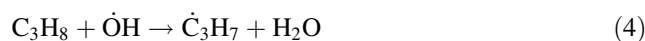
Formation of OH radical,

$$O_3 \xrightarrow{hv} \dot{O} + O_2 \qquad (1)$$

$$\dot{O} + O_2 \xrightarrow{M} O_3 + M \qquad (2)$$

where M is a third body present in air

$$\dot{O} + H_2O \rightarrow 2\dot{O}H \qquad (3)$$

Formation of photochemical ozone from NMHCs and NO_x,

$$C_3H_8 + \dot{O}H \rightarrow \dot{C}_3H_7 + H_2O \qquad (4)$$

$$\dot{C}_3H_7 + O_2 \rightarrow C_2H_7\dot{O}_2 \qquad (5)$$

$$N\dot{O} + C_2H_7\dot{O}_2 \rightarrow NO_2 + C_2H_7\dot{O} \qquad (6)$$

$$NO_2 + hv \xrightarrow{\lambda \leq 420\,nm} N\dot{O} + \ddot{O} \qquad (7)$$

$$\ddot{O} + O_2 \rightarrow O_3 \qquad (8)$$

Ground level ozone is a very important secondary pollutant formed by the photochemical reaction of various

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primary pollutants. It is considered to be a potential green house gas, and a strong oxidant thus having an adverse effect on plants, humans, materials and the entire ecosystem [7–10]. In addition to the tropospheric ozone formation, NMHCs also play an important role in the production of secondary organic aerosol (SOA) and some other organic nitrates [3, 5]. Initial NMHCs measurements were reported at various industrial locations in Mumbai, a mega-city and a major petrochemical hub in western part of India [11]. This was followed by several campaign mode studies over urban and rural locations in western, central and northern India as well as over the Bay of Bengal (BoB) and Indian Ocean reporting a pronounced seasonal variation in NMHCs concentration [12–17]. Subsequently C_2–C_5 NMHCs were determined in a year long study conducted during the year 2012–2013 over Kolkata, a mega city in the eastern part of India [18]. These species have been observed to originate from both anthropogenic and biogenic sources that include fossil fuel combustion, natural gas leakage, fuel storage and transportation, biomass burning, gasoline evaporation and solvent usage, emission from vegetation as well as geochemical processes [19, 20] and have a major sink due to their reactivity with OH radicals [21]. Ample OH radicals have lead to maximum surface ozone formation over the tropics [22, 23].

As per previous reports of rise in surface air pollutant concentration at Bhubaneswar during winter months [23, 24] an attempt has been made to study the distribution of C_2–C_5 NMHCs along with the photochemical activity of the species during December 2013–February 2014. Though winter is not a prominent season over the location, however the concentration of several air borne pollutants is observed to be more pronounced due to a stable atmospheric condition and long-range transport from Indo-Gangetic plains (IGP). This investigation gives a preliminary impression about the NMHCs measurements in the eastern coastal part of India, which is a strategic location for monitoring IGP outflow into the Bay of Bengal [25–27]. Therefore the results of this study are expected to provide a platform for future investigations on surface ozone formation potential in tropical climate with respect to NMHC chemistry. Keeping in view the important role played by NMHCs in tropospheric photochemistry of various secondary pollutants, further in depth studies needs to be carried out in more locations over India.

2. Experimental Details

2.1. Site Description

The sampling site is laboratory of Council of Scientific and Industrial Research-Institute of Mineral and Material Technology (20°30′N, 85°83′E, altitude of 45 m asl) which
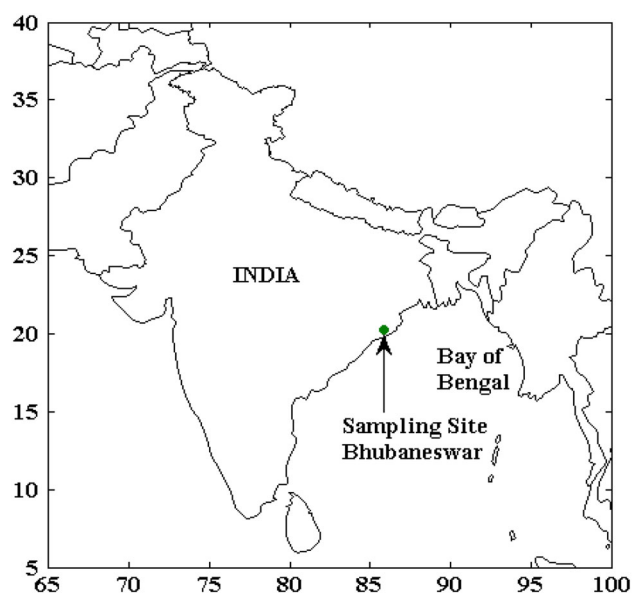

Fig. 1 Indian map showing the sampling site

is located in the capital city of Odisha state, Bhubaneswar (Fig. 1). Odisha is a coastal region having tropical warm climate and is believed to be a major source of OH radicals due to higher levels of water vapour and solar radiation [28]. Bhubaneswar is considered to be one of the fastest growing cities in the eastern part of the country. The station has distinct weather conditions during various seasons of the year like pre-monsoon (March–May), monsoon (June–Aug), post-monsoon (Sept–Nov), and winter (Dec–Feb). Average temperature ranges between a minimum of around 10 °C to a maximum of 20–25 °C. During winter the city receives chilly winds from the N and NE at an average speed of 7 miles/h and the temperatures drop to approximately 15 °C. The city has a population of 1.2 million and is surrounded by small townships (approximately within 100 km) where various mining and fertilizer based industries are operational.

2.2. Sample Collection for NMHCs

Air was siphoned (using a Sensidyne low flow sampler (model LFS-113D)) into a PerkinElmer make Air-toxic tube that uses solid adsorbent for trapping ambient NMHCs within them. These tubes are then placed in the GC for further analysis.

Samples were collected between 9:00 am and 6:00 pm (IST) at regular interval of 1 h, twice a week only (during the weekdays) throughout the measurement period (1st December 2013 till 28th February 2014). The measured NMHCs species are ethane (C_2H_6), ethylene (C_2H_4), propane (C_3H_8), propylene (C_3H_6), n-butane (C_4H_{10}), acetylene (C_2H_2) and pentanes (C_5H_{12}). In order to study the diurnal variation of NMHCs, ambient air samples were collected on three representative days

of each month at an interval of 3 h. The statistical significance of the given measurements has been discussed in the later section.

2.3. Analytical Procedure for NMHCs

The experimental system consists of a PerkinElmer Clarus® 480 Gas Chromatograph (GC) equipped with a flame ionization detector (FID) and a 30 m × 0.53 mm Elite-Alumina capillary column for NMHCs analysis. Ambient air samples of 3000 ml collected in the air toxic tube were pre-concentrated using a Turbo Matrix Thermal Desorbers (TD). High purity Helium (He) gas was used as carrier. The trap uses two adsorbents; the weaker (carbon black) adsorbent is towards the sample inlet/outlet and will retain the less volatile analytes from the sample. The stronger (carbon molecular sieve) adsorbent is positioned behind the weaker adsorbent to catch the most volatile analytes (C_2–C_4). When the trap is heated, the desorbed analytes are back flushed from the trap. This ensures that the less volatile compounds never make a contact with the stronger adsorbent (Fig. 2).The trapped analytes are thermally desorbed and carried through a heated transfer line. After pre-concentration the sampling loop was heated to 125 °C and the sample was automatically injected into the column. Once the first sample has been collected and injected into the GC, the trap automatically cools to −30 °C and is ready for the next sample. Calibration of individual NMHCs were performed using a standard gas mixture provided by Alchemie Gases & Chemicals (Certified by TUV India Private Limited) and further calibrated using National Institute of Standards and Technology (NIST) traceable standard gases provided by the Linde group (USA) [29, 30].

2.4. Measurement of CO, Ozone and Meteorological Parameters

Continuous measurements of surface ozone and CO are being made on the roof top of the Institute of Minerals and Materials Technology (IMMT), Bhubaneswar using online
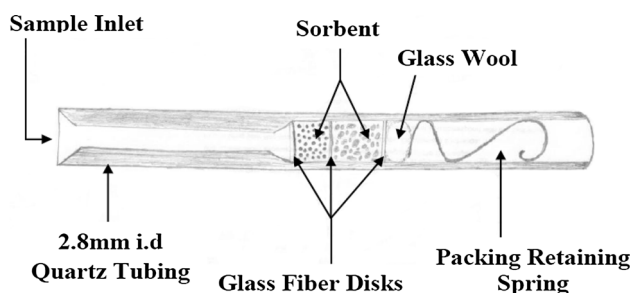

Fig. 2 Internal geometry of the PerkinElmer Air Toxics Trap

analyzers i.e. ozone (Thermo Scientific Model 49i) and CO (HORIBA APMA-370) since 2009 and 2011 respectively. Ozone analyzer uses UV Photometric technology for measurement of ambient ozone and is calibrated using internal ozonator along with zero gas while CO analyzer is based on the principle of Non-dispersion cross modulation infrared analysis method and calibrated using NIST traceable standard gas through the help of a dynamic gas calibrator [31] (Thermo Scientific 146i). More details regarding the measurement and instrumentation techniques have been described elsewhere [25]. Meteorological parameters are measured using an automatic weather station (AWS) RainWise, Inc (CC-3000) which is regularly calibrated and data acquisition frequency at 15 min interval. These data are also being validated with data of IMD (Indian Meteorological Department), Bhubaneswar from time to time.

3. Results and Discussions

3.1. General Characteristics of NMHCs in Bhubaneswar

Eight C_2–C_5 light non methane hydrocarbons have been measured at Bhubaneswar for a period of 3 months (December 2013–February 2014). The average mixing ratios and their standard deviations for the individual NMHCs are shown in Table 1. A comparison has also been shown with the NMHCs species measured at other locations in India and some other part of Asia (Table 1). It is observed that concentration of NMHCs over Bhubaneswar is less than most of the urban sites of India and other countries while it is higher than that observed over the BoB. Propane is found to be the dominant species having highest concentration of 1.53 ppbv indicating higher levels of LPG emissions in the city. Then n-pentane is the second dominant species (0.83 ppbv) followed by i-pentane (0.47 ppbv) and propylene (0.21 ppbv).

3.2. Statistical Analysis

One way Analysis of Variance (ANOVA) has been used in the current study to determine whether month wise TNMHCs concentration has any significant variation or not. In order to determine the same we have used the null hypothesis technique. This technique suggests that if F value (calculated) is ≤critical values then it is assumed that there is no variation and vice versa [28].

In the present analysis a p value of 0.072429 suggests that the analysis has confidence level of 97 %. Based on the f-calculated (3.075698) and f-critical (3.591531) values it can be determined that variation in concentration of

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Table 1 Average mixing ratios of NMHCs (ppbv) measured at Bhubaneswar and compared with the measurements made in other locations of India and some other parts of world [4, 11–13, 15, 16, 25, 27, 43, 44, 45]

NMHCs Species	IMMT Dec 2013–Feb 2014	Kolkata Mar 2012–Feb 2013	Mt. Abu 2002	Hyderabad 2010	Mumbai Mar 1993–May 1994	Kanpur Dec 2004	Hissar Dec 2004	Ahmedabad 2002 (Online)	Guangzhou, China 2005	Happo, Japan Dec 1998–Feb 1999	N-BoB
Ethane (C_2H_6)	0.102 ± 0.036	3.9 ± 3.4	1.2 ± 0.6	28.3	1.3	9.53 ± 3.63	7.94 ± 3.58	3.7 ± 3.7	3.15 ± 2.89	1.914 ± 0.388	1.734 ± 0.146
Ethylene (C_2H_4)	0.049 ± 0.027	4.5 ± 2.5	0.3 ± 0.2	3.1	2.3	8.82 ± 4.64	7.52 ± 5.46	2.9 ± 2.6	2.79 ± 1.45	0.366 ± 0.046	0.129 ± 0.055
Acetylene (C_2H_2)	0.016 ± 0.016	3.7 ± 2.5	0.4 ± 0.4	2.6	1.1	5.48 ± 2.46	4.29 ± 2.42	2.0 ± 1.9	5.46 ± 4.03	0.633 ± 0.051	0.655 ± 0.241
Propane (C_3H_8)	1.532 ± 0.782	8.4 ± 5.6	0.5 ± 0.2	3.5	5.6	3.97 ± 2.43	3.07 ± 1.99	4.4 ± 2.9	4.49 ± 3.69	0.79 ± 0.233	0.170 ± 0.204
Propylene (C_3H_6)	0.208 ± 0.131	1.8 ± 1.7	0.2 ± 0.1	–	0.2	2.2 ± 1.47	2.34 ± 1.94	1.0 ± 0.9	2.26 ± 2.10	0.018 ± 0.005	0.071 ± 0.032
n-Butene (n-C_4H_{10})	0.027 ± 0.019	6.3 ± 5.0	0.3 ± 0.3	2.4	16.4	2.33 ± 1.85	2.12 ± 1.89	2.8 ± 2.4	2.54 ± 1.80	0.338 ± 0.89	0.118 ± 0.084
i-pentane (i-C_5H_{12})	0.468 ± 0.498	3.2 ± 2.2	–	7.7	–	2.05 ± 7.85	1.13 ± 2.1	1.9 ± 2.4	1.81 ± 1.70	0.167 ± 0.022	–
n-pentane (n-C_5H_{12})	0.831 ± 0.601	–	–	–	–	1.06 ± 2.82	0.72 ± 0.84	–	1.18 ± 0.97	0.126 ± 0.022	–

TNMHCs during the 3 months of winter season is non-significant as f-calculated value is less than f-critical.

3.3. Diurnal Variation

The diurnal variation of C_2–C_5 NMHCs is shown in Fig. 3. Bi-modal peaks were observed for ethane as well as ethylene during morning (6.00–9.00 am) and evening (6.00–9.00 pm) hours corresponding to higher traffic volumes [32]. Diurnal variation of propylene was also attributed to vehicular exhaust. Lower concentrations of these species observed during noon may be due to the oxidative reaction with OH radical which is at its peak during the same period [33]. Another reason for the above variation is because of the dispersion of air pollutant due to the increase in planetary boundary layer (PBL) height with increase in temperature during mid day.

In India Liquefied Petroleum Gas (LPG) is used as a common cooking fuel with propane and butane as the two major components. Since the emission source is considered to be independent of air temperature therefore, the highest concentration of both propane and butane between 9:00 am and 12:00 pm IST may be inferred to the wide use of LPG gases in the city [34].

i-pentane and n-pentane were observed to be higher during the afternoon (12–15 pm IST) which is completely reverse to the diurnal variation trend of pentanes measured at other sites of India [12], where bi-modal peaks were observed during morning and evening hours. This implies that only vehicular emission may not be a major contributor of these two species, rather the dominant source of i-pentane and n-pentane may be the contribution from gasoline or solvent evaporation [35, 36]. The measurement site being a scientific laboratory, solvents are very commonly used for experimental purposes which may be a potential source of the pentanes during day time. Further, an increase in air temperature during noon also favors solvent evaporation [37]. A long term measurement would probably bring more clarity regarding the different sources of NMHCs however presently it is beyond the scope of this study.

3.4. Interspecies Correlation Between NMHC Species

NMHCs, being primary pollutants in the atmosphere, are always concomitant with the emissions near the source region. There are various anthropogenic sources of light NMHCs and an inter-species correlation would provide important information about their common dominant sources

A good correlation between n-pentane versus i-pentane ($R^2 = 0.66$) indicate their common source of emission from solvent evaporation (Fig. 4) [25]. Also, as mentioned
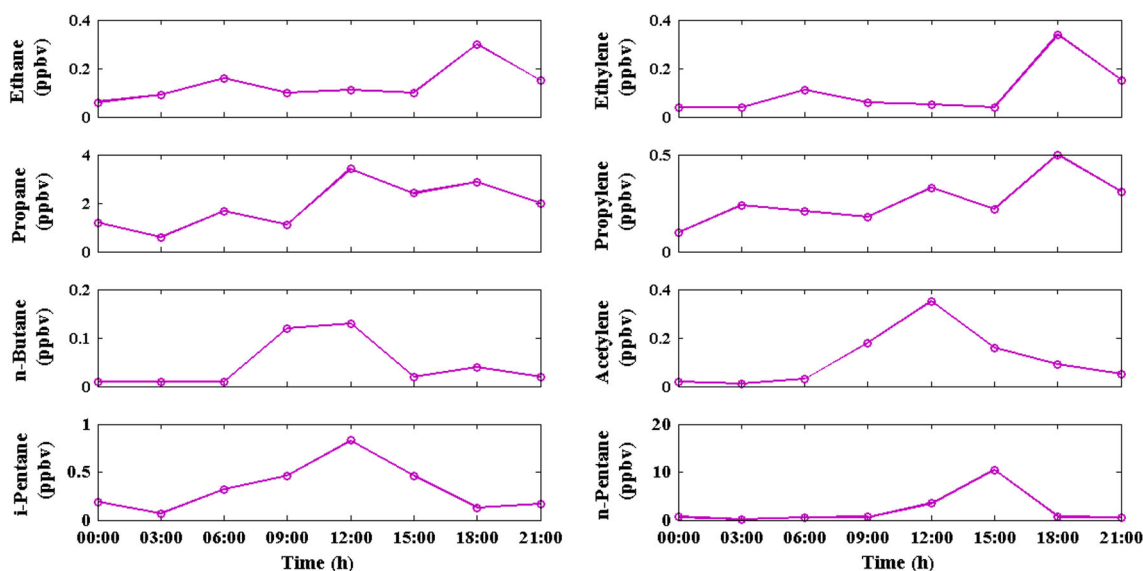
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Fig. 3 Diurnal variation of C₂–C₅ NMHCs at Bhubaneswar, India

earlier, our laboratory specializes in mineral and material research which make use of various organic solvents resulting in higher concentrations of *n*-pentane and *i*-pentane. Correlation of ethane versus ethylene ($R^2 = 0.50$) suggests similar sources of emission from vehicular sources as has been discussed in earlier section based on their diurnal variation. The correlation study between propane versus *n*-butane ($R^2 = 0.66$) suggests related sources of emissions mostly from LPG usage, which is a common fuel in most of the urban areas of India [34]. Again correlation between acetylene versus *n*-butane ($R^2 = 0.62$) suggests a similar source of emission. These correlation between propane versus *n*-butane and acetylene versus *n*-butane indicates that *n*-butane might be generated from two major sources i.e. fossil fuel combustion and LPG leakage [32]. Moderate or relatively low correlation coefficient values of 0.44, 0.23 and 0.23 for *n*-butane versus *i*- pentane, *n*-butane versus *n*-pentane and propane vs propylene respectively, indicate that these species originate from different sources.

3.5. The Photochemical Reactivity of NMHCs

The impact of NMHCs on various tropospheric chemical reactions is related to their concentration and OH reactivity. More reactive NMHC species contribute higher to the total photochemical ozone concentration. In general alkenes are more reactive compared to alkanes. To estimate the reactivity of individual NMHCs, the propylene-equivalent concentration (Prop-Equiv) were determined to be a better indicator and it was calculated using Eq. (9) [38].

The Prop-Equiv (*i*) of hydrocarbon *i* is defined as:

$$\text{Prop-Equiv }(i) = \frac{\text{Conc. }(i) \times k_{\text{OH}}(i)}{k_{\text{OH}}(\text{propylene})} \tag{9}$$

where Conc. (*i*) is the concentration of hydrocarbon '*i*' expressed in ppbc, $k_{\text{OH}}(i)$ and $k_{\text{OH}}(\text{propylene})$ are rate constants for the reaction of hydrocarbon '*i*' and propylene with OH respectively. Prop-Equiv (*j*) is a measure of the concentration of species '*i*' (ppbC) on an OH-reactivity based scale normalized to the reactivity of propylene.

The mechanism of ozone formation for each different NMHCs differs from each other significantly. In order to investigate the contribution of non-methane hydrocarbons to the production of photochemical ozone, the ozone formation potential (OFP) were calculated. OFP can be estimated as the product of the concentration of NMHCs and the MIR coefficient (gram of ozone produced per gram of hydrocarbon '*i*'). Equation (10) was used to calculate the OFP by each hydrocarbon under optimal conditions:

$$\text{Ozone formation potential OFP }(i) = \text{Concentration }(i) \times \text{MIR coefficient }(i) \tag{10}$$

where MIR is the maximum incremental reactivity [39, 40]. Table 2 shows the photochemical reactivity of the measured NMHCs with the OH radical and also their contribution to the photochemical ozone in the measurement site. The study reveals that alkenens contribute more to the total OFP than alkanes. Among all the measured NMHCs, propylene has the highest potential towards photochemical ozone formation (3.366 μg/m³) accounting for about 34 % of total OFP. This further indicates a major contribution of vehicular emissions to the photochemical ozone at Bhubaneswar. *n*-Pentane is the second highest
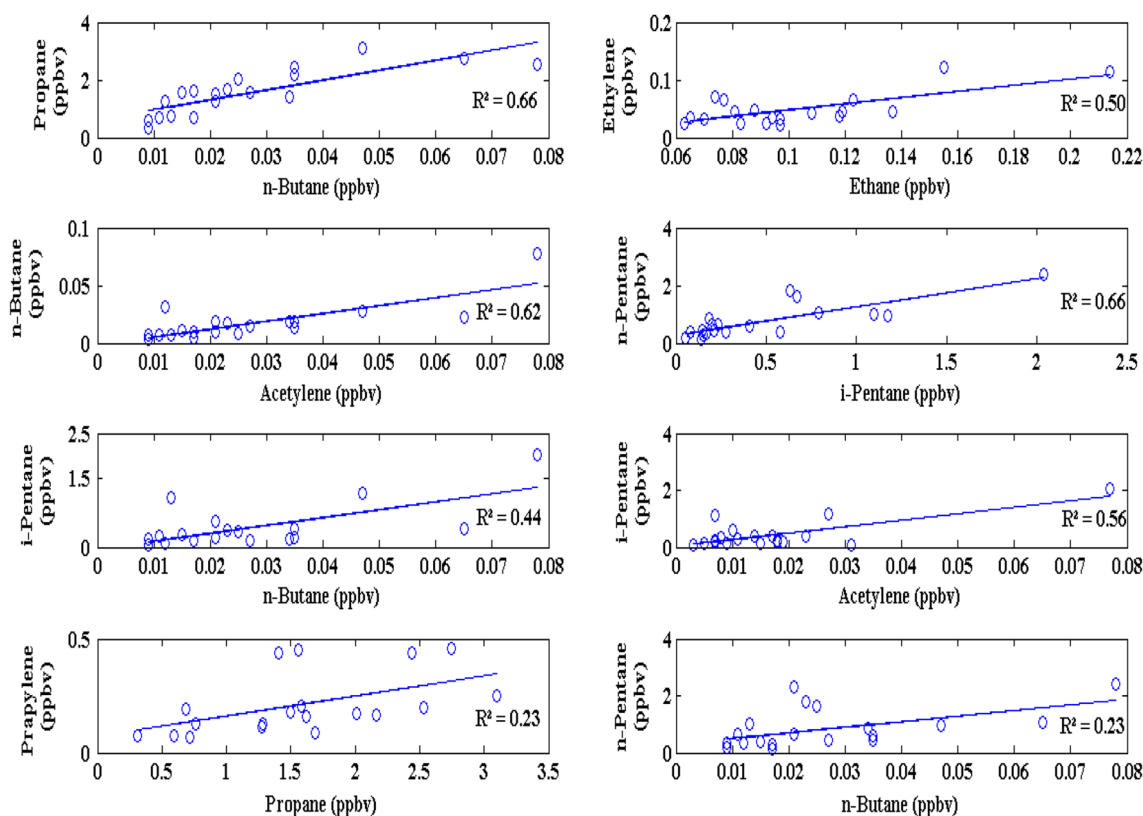
Fig. 4 Interspecies co-relationship of measured NMHCS

Table 2 Photochemical properties of C_2–C_5 NMHCs in Bhubaneswar

NMHCs	ppbc	($\mu g/m^3$)	Rate constant with OH	MIR	Prop-Equiv (ppbc)	OZONE formation ($\mu g/m^3$)
Ethane	0.203	0.125	0.26	0.25	0.002	0.032
Ethylene	0.098	0.056	8.52	7.4	0.029	0.415
Propane	4.597	2.763	1.15	0.48	0.184	1.327
Propylene	0.624	0.358	26.30	9.4	0.624	3.366
n-butane	0.106	0.065	2.54	1.02	0.010	0.067
Acetylene	0.066	0.018	0.79	0.5	0.002	0.009
i-pentane	2.34	1.381	3.60	1.38	0.351	1.906
n-pentane	4.153	2.452	3.94	1.04	0.623	2.551

contributor (2.551 $\mu g/m^3$) i.e. around 26 % which is mainly from gasoline and solvent evaporation. This is also an important contributor to the ozone formation followed by *i*-pentane (1.906 $\mu g/m^3$) about 19 % and ethylene (0.415 $\mu g/m^3$) about 4 % to the total OFP. MIR coefficients were taken from Carter [39].

3.6. Variation of NMHCs with Relative Humidity

Being a primary pollutant, the concentration of TNMHCs were observed to be strongly influenced by the local meteorological parameters during the sampling period.

Figure 5 shows the daily average variation of relative humidity with TNMHCs during the sampling days.

TNMHCs show an inverse correlation with relative humidity with R^2 value of 0.34, which may be due to the reduction reaction of NMHCs with OH radical [5, 41]. This is again an evidence of the precursor relationship between NMHCs and photochemical ozone.

3.7. Variation of TNMHCs with CO and Ozone

The concentration of surface ozone and CO have been measured during the sampling period. Figure 6 shows the
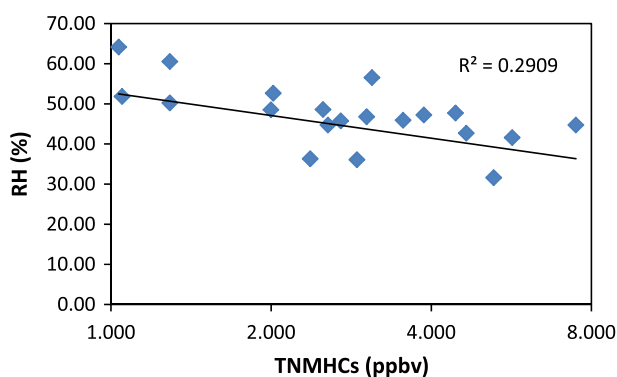
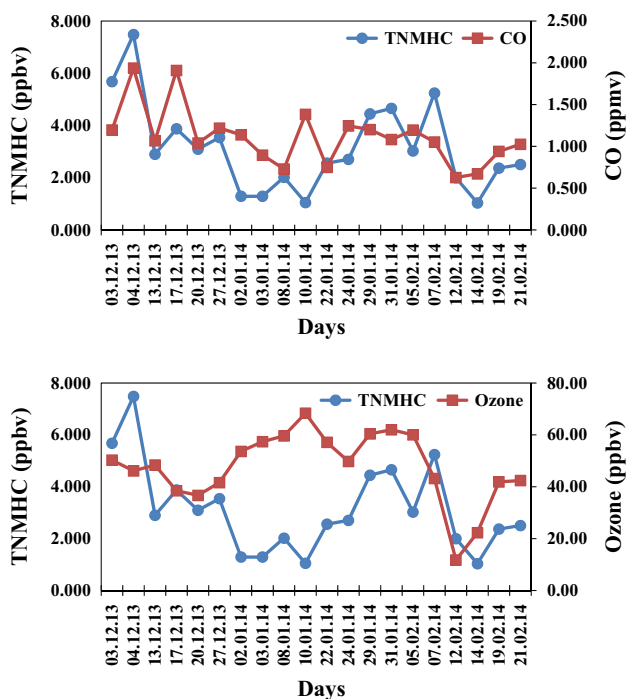**Fig. 5** Variation of TNMHCs with RH

Fig. 6 Variation of TNMHCs with CO and ozone

daily averaged variation of TNMHCs with CO and ozone. Distribution of TNMHCs show a distinct inverse variation as compared to ozone. This is due to the photooxidation of NMHCs with atmospheric OH radicals.

Almost similar variation of CO with TNMHCs indicates their common source of emission from the traffic volume, because in most of the urbanized areas the predominant source of CO is from automobile exhaust generated due to the incomplete combustion of fossil fuel [42].

4. Conclusions

The current study gives an overview of initial measurement of light NMHCs during winter months at Bhubaneswar and highlights their photochemical reactivity. Propane was the largest contributor to the TNMHCs concentration whereas propylene was observed to have the highest OFP in the particular location. RH had a profound influence in reducing TNMHC concentration. It was also observed from the diurnal studies that propane and butane were mostly associated with LPG emissions in Bhubaneswar. Vehicular emissions had a major contribution to the TNMHCs over the site whereas solvent usage was found to be an important source of *i*-pentane and *n*-pentane. Daily average variation of TNMHCs and ozone proves its precursor relationship while TNMHC and CO concentrations depicts similar sources. Statistical studies of the observed data showed an insignificant variation between the different months during the winter season suggesting robustness of the study. The average mixing ratio of NMHCs over the site were observed to be lower in comparison to other urban locations in India.

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