เกณฑ์ความเข้มข้น Total Non-methane Hydrocarbon ในเมือง Nagpur ตอนกลางของประเทศอินเดีย

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Research Article

Diurnal-, Seasonal- and Site-Dependent Variability in Ground-level Total Non-Methane Hydrocarbon in Nagpur City of Central India

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ABSTRACT Temporal & spatial variations in ground-level total non-methane hydrocarbon (TNMHC) were studied in Nagpur urban agglomeration (UA) for a year over three seasons viz. post-monsoon (September–October), winter (January–February) and summer (May–June) in 2013–14. Ground-level TNMHC showed low to moderate spatial (over residential, commercial, traffic intersections, residential cum commercial sites) and temporal (at 7:00, 13:00; 18:00 and 23:00 h in all three seasons) variations. There was no specific increasing or decreasing trend with time, either within a day or a season. Daily mean concentration of TNMHC (averaged over concentrations at 7:00, 13:00; 18:00 and 23:00 h) ranged from 0.88–1.73 ppmV, 1.75–4.04 ppmV and 1.20–1.53 ppmV at residential sites; 2.99–6.47 ppmV, 1.52–7.38 ppmV and 0.98–1.63 ppmV at traffic site; 0.83–1.15 ppmV, 2.03–3.24 ppmV, 1.1–1.70 ppmV at residential cum commercial sites and 1.05–4.79 ppmV, 6.2–8.58 ppmV, 0.34–0.64 ppmV at the purely commercial site, during post-monsoon, winter and summer, respectively. Occasional spikes (TNMHC $>$ 10 to $<$ 13.6 ppmV) were observed on three occasions over two sites in winter but reasons thereof remained unidentified. During Diwali Festival (in post-monsoon) marked by large-scale firecrackers bursting, observed TNMHC concentrations hovered around 3–5 ppmV, which almost matched with 90th percentile of other post-monsoon concentrations. Highest mean seasonal TNMHC concentration was observed during winter, followed by means of post monsoon and summer seasons while mean ground-level TNMHC concentrations on weekdays were slightly higher (1.17–1.21 times) than weekends over all seasons.

KEY WORDS Air pollution, NMHC, Urban, VOC, Weekend

1. INTRODUCTION

Non-methane hydrocarbons (NMHCs) together comprise major group of organic pollutants (Caselli *et al.*, 2010; Xiao and Zhu, 2003) that are actively involved in atmospheric photochemical reactions (Mudliar *et al.*, 2010; Elbir *et al.*, 2007). The NMHCs are constituents of volatile organic compounds (VOC) that have short atmospheric lifetimes (fractions of a day to months) and have direct but small impacts on atmospheric radiative forcing (Intergovernmental Panel on Climate Change; https://www.ipcc.ch/ipccreports/tar/wg1/140.htm). NMHCs may also have serious health effects like neurosis and dementia among others (Kandyala *et* *al.*, 2010; Filley *et al.*, 2004; Chen *et al.*, 1994). High reactivity of NMHCs enables them to produce tropospheric ozone (O_3) through reactions with nitrogen oxides (NO_x) and radicals. As NMHCs have certain influence on O_3 formation, controlling NMHC emissions assumes significance and has been imposed to attain O_3 standards (Batterman *et al.*, 2005). In rural areas, where NO_x concentration is generally low, O_3 generation is also less, but in polluted urban locales, presence of low ambient NMHCs might lead to substantial O_3 production under significant NO_x levels (Donahue and Prinn, 1990). NMHCs are thus well known agents of O_3 precursor through the involvement of OH radical and NO_x (Warnec, 1988). World Meteorological Organization Global Atmospheric Watch (WMO/GAW) programme undertakes measurements on NMHCs and other reactive compounds in global network (WMO, 2007).

Gasoline filling stations, open-waste burning practices, LPG leakages, solvents and vehicular emissions are the primary anthropogenic sources of NMHCs in urban air (Duan *et al.*, 2008; Tang *et al.*, 2007). Also, power and petrochemical plants, refineries, chemical plants, painting operations, varnishes, coating operations, consumer products, cold clean degreasing, printing inks, dry-cleaning and solid waste disposal are other sources (Srivastava and Mazumdar, 2011; Barletta *et al.*, 2002; Arya, 1999). Vehicular emission is one of the major NMHC sources and their emissions from vehicles include refuelling losses, starting emissions, evaporative losses and tailpipe emissions (Batterman *et al.*, 2005). As per Tan *et al.* (2011), i-pentane, ethene, ethane, ethyne, toluene and propane were the primary hydrocarbons (HCs) in Foshan in China. Generally, most abundant HCs exhibited high concentration in morning, dipped to the lowest level in afternoon and increased to higher values in evening hours. But, i-pentane exhibited highest level in afternoon, indicating accelerated solvent evaporation in higher temperature. Vehicular emissions were the main source of propene, i-butene, isoprene, ethene, benzene and toluene and n-pentane, n-hexane, and n-heptane came from petrol evaporation. LPG leakage could have been the main source of propane, while leakage of natural gas was source of ethane in Foshan City (Tan *et al.*, 2011). Potential sources of greenhouse gases and air pollutants in Nagpur Urban Agglomeration (UA) has been discussed before (Majumdar *et al.*, 2013; Majumdar and Gajghate, 2012) and some of these sources are also potential emitters of NMHCs in Nagpur city.

Monitoring of total NMHC (also known as TNMHC) concentrations in ground-level air has been undertaken sparsely from a few Indian cities (Sharma *et al.*, 2016; Sarkar, 2015; Nishanth *et al.*, 2014) and there are some reports on ambient concentrations of select individual NMHCs and VOCs from a few Indian locations (Srivastava and Mazumdar, 2011; Purkait *et al.*, 2009; Sahu and Lal, 2006a, b). Knowledge on ground-level TNMHC concentrations could actually help formulate air quality management planning of a city. Indian cities could be potential hotbeds of NMHCs due to variety of NMHC sources like vehicular traffic consisting of sizeable fleet of old vehicles, fossil fuel burning in household and commercial sector, small manufacturing units, painting and varnishing workshops, petrol pumps, auto refinishing workshops etc. and therefore, it is important to assess ground-level TNMHC concentrations over Indian cities. This work was undertaken to measure TNMHC in ground-level air of Nagpur, one of the major and progressive cities of Central India over post-monsoon (September–October), winter (January–February) and summer (May–June) during 2013–2014 in a year-long study. Temporal (diurnal and seasonal) and spatial variation in TNMHC *vis a vis* the abundance of reported sources over the selected UA has been examined and reported. Also, mean TNMHC concentrations during weekdays and weekends over all the seasons were calculated, evaluated and compared.

2. RESEARCH METHODS

2. 1 Background of Study Area and Potential Sources of NMHCs

The study was conducted in Nagpur city within Maharashtra State of India. As per Govt. of India's last Census data in 2011, Nagpur is an Urban Agglomeration (UA)/city with a Million Plus population (2,122,965). It is the largest UA/city in Central India and by population, 3rd largest in State of Maharashtra. Nagpur District has an area of about 9897 sq. km. while Nagpur UA/city encompasses about 217.65 sq. km. (Nagpur Municipal Corporation 2006). National highways NH-7 and NH-6 and Asian highways AH-43 and AH-46 pass through Nagpur (Bhonsle, 2010) and carry significant load of commercial and personal vehicles.

Nagpur has a variety of potential sources of NMHCs. A detail reconnaissance was conducted to make an inventory of prominent sources of NMHCs (Table 1). Some of these sources like thermal power plants and industries could potentially contribute to TNMHC in ground-level air of Nagpur through local and regional dispersion, although some of the sources are located beyond 10 km of the nearest air quality monitoring sites. Prevailing season is also expected to have a direct role to play on relative predominance of specific sources by influencing activities like open burning, domestic heating/cooling, tourist influx and festivities.

Suitable sites for collection of ground-level air samples for estimations of NMHCs were scouted by a thorough analysis of city map followed by reconnaissance, delineating various residential, commercial, market areas and important traffic intersections and roads. Inventory was made on various potential sources of NMHCs during reconnaissance. It was observed that there was conspicuous overlapping of various important activities viz. vehicular movements, commercial activities, sporadic biomass combustion, residential activities, cooking by fossil fuels in restaurants and mobile streetside food stalls, operation of petrol pumps etc. at several sites that could affect diurnal and seasonal air quality in terms of NMHCs. Therefore, selected sites could only be classified into (i) Residential (ii) Purely commercial (iii) Traffic intersections and (iv) Residential cum commercial, based on major activities in and around the sites. The sites in Nagpur study area is presented in Fig. 1.

2.2 Sampling and Analysis of TNMHC

Sampling for ground-level air was undertaken over 2 months during summer (May–June), post-monsoon (September–October) and winter (January–February) seasons in 2013–14. Ground-level city air at about 1.5 m above ground level was collected at different time periods of a day (08:00 h, 13:00 h; 18:00 h and 23:00 h) over about three weeks in each season to capture diurnal and spatial variations. The samples represented city's ground-level air which was influenced by direct emissions from an ensemble of abundantly available NMHC sources, most of the sites being active in-terms of anthropogenic activities like cooking in roadside eateries, movement of vehicles, presence of petrol pumps (in a few areas), environmental tobacco smoke in congested areas (especially in commercial and traffic intersections) etc. TNMHC was analyzed in the ground-level air samples collected in

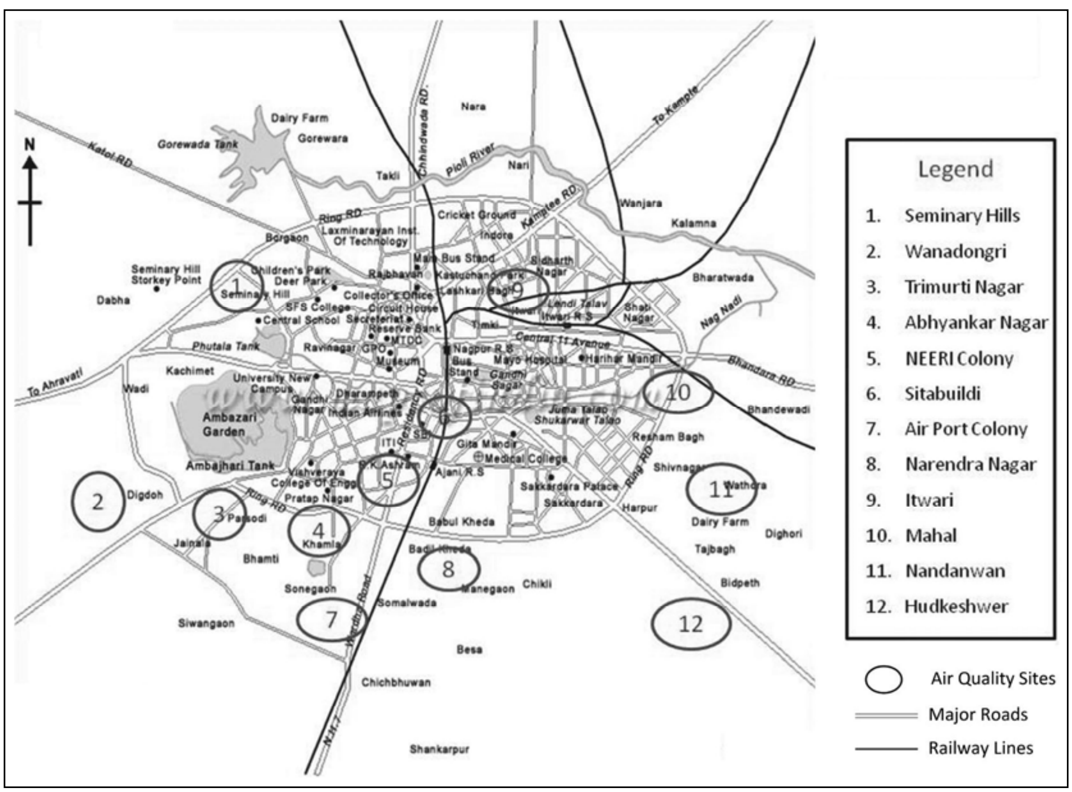

Fig. 1. Locations of the selected air quality monitoring sites in Nagpur city (Map Source: Compare Infobase Pvt. Ltd.).

Table 1. Inventory of potential sources of non-methane hydrocarbons (NMHCs) in Nagpur city.

Source	Predominant NMHCs sources in Nagpur	Sites affected
Industries	Nagpur city is fringed by Butibori Industrial Area and Hingna Industrial Estate, which have industries like chemicals, rubber, paints, polymer etc. These industries are potential emitters of NMHCs.	Wanadongri (Residential + Commercial)
Power plants	Two coal-fired super thermal power stations (STPS), namely the 840 MW Khaparkheda STPS and the 1080 MW Koradi STPS adjacent to Nagpur are potentially big emitters of NMHCs. The selected sites are far away from these plants, nearest one being about 12 km away (Itwari).	No air quality site was near ($<$10 km) to this source
Vehicular traffic	Nagpur has National highways NH-7 and NH-6 passing through apart from two Asian Highways AH43 and AH46. Auto rickshaws running on mixtures of petrol and kerosene are the main form of hired transport within the city along with private vehicles and buses. About 4.6 lakh registered vehicles are there in Nagpur including 2-wheelers, 3-wheelers and 4-wheelers. Total length of city roads was 1907 km in 2002–2003 (Nagpur Municipal Corporation, 2006).	Itwari (Commercial), Sitabuldi (Traffic), Hudkeshwar Road and Wanadongri (Residential + Commercial)
Domestic cooking	Domestic sector in Nagpur consists of residential colonies, urban slums, semi urban and rural population. Apart from LPG, sizeable quantity of low-grade coal, kerosene and wood are used for domestic combustion due to their easy availability and low cost, significantly influencing NMHC emissions from Nagpur (Majumdar and Gajghate, 2011).	NEERI Colony, Abhyankar Nagar, Narendra Nagar, Trimurti Nagar, Nandanwan, Mahal (All Residential)
Commercial cooking	Apart from LPG being the primary fuel, low-grade coal, charcoal cow dung, fuelwood, coal balls etc. are used by the organized and unorganized restaurant sectors in Nagpur (Majumdar *et al.*, 2013) which all are potential sources of NMHCs.	Itwari (Commercial), Sitabuldi (Traffic), Hudkeshwar Road and Wanadongri (Residential + Commercial)
Sewage channels	Sewage channels and severely polluted Nag River running through Nagpur could be a potential source of NMHCs.	Nandanwan, Mahal, Hudkeshwar Road (Residential), Sitabuldi (Traffic)
Aircrafts	Dr. Babasaheb Ambedkar International Airport could be a significant source of NMHCs due to aviation fuel loading and storage activities. Over twenty passenger aircrafts operate from this airport everyday catering to about 4000 passengers per day (Nagpur Airport, http://www.nagpurairport.com/). Nagpur also has an Indian Airforce Maintenance Command.	Airport Colony (Residential)
Waste burning	Sporadic open burning, especially in winter to fight off cold, could be responsible for NMHC emissions in various parts of the city.	Difficult to designate, as this source is unregulated and sporadic
Waste dumps	Waste generation was estimated to be 650 tons per day (TPD) (http://www.cpcb.nic.in/divisionsofheadoffice/pcp/MSW_Report.pdf, accessed on 27.9.17) in Nagpur city during 2004-05. The city had a population of about 2,405,421 as per 2011 census (http://www.census2011.co.in/census/city/353-nagpur.html) signifying the likely extent of solid organic waste generation in future. Bhandewadi dump yard in Nagpur handles MSW in about 22 hectares land while about 20 hectare land is used for composting (Akolkar *et al.*, 2008).	No site is near (within 5 km) to this source except Nandanwan (Residential)
Petrol pumps	Nagpur city has about 38 auto petrol filling stations (http://automobiles.mapsofindia.com/petrol-stations/nagpur.htm, accessed on 27.9.17) that also are potential emitters of NMHCs.	Itwari (Commercial), Sitabuldi (Traffic), Hudkeshwar Road and Wanadongri (Residential + Commercial)

Tedlar bags (SKC Inc., USA) as specified by ASTM-D6345-98 by passive filling up for about 30 minutes. Some of the sites, as described above, were directly inside heavy traffic or commercial activities in the heart of the city and being just above ground level, were directly under the heavy influence of ground level NMHC emissions. TNMHC was determined by a Hydrocarbon Analyser (Model HC51M, Environment, SA) within 12 hours of sample collection. This analysis is based on flame ionization detection of hydrocarbons (0–1000 ppm). The analyzer was fitted with a FID housed in oven with a column that separated methane from TNMHC. The gas samples pass at 1.4 L/min flow rate through a specially layered packed column wherefrom CH_4 is fed first into the detector. Subsequently, the column is back-flushed and other hydrocarbons are passed into the detector, resulting in two quantifications, one of them being the TNMHC. Instrument calibration was undertaken by CH_4-free zero air for zeroing and a standard certified NIST traceable 10000 ppb hydrocarbon (as isobutylene) in Air balance (Chemtron Science Laboratory, Mumbai) with certification accuracy of ±1%. Lowest detectable limit (LDL) of the instrument was 0.05 ppm HC while zero drift was 0.2 ppm and span drift was <1% over 7 days. The uncertainty of the standard deviation of measurements, related to the dispersion of results (U_{disp}) was calculated by the following expression:

$$U_{disp} = s(q)/(n)^{1/2}$$

where s(q) is the standard deviation and n is the number of readings (Madeira *et al.*, 2009). The U_{disp} for TNMHC measurement by the instrument was estimated to be 0.1257.

2.3 Meteorological Data

Temperature, relative humidity, wind direction and speed that govern ground-level concentrations, distribution and dispersion of NMHCs over the UA were collected to support air quality data on TNMHC. Nagpur's meteorological data was collected from online data archived at wunderground.com that uses meteorological data received from the meteorological station of Indian Meteorological Department (IMD) in Nagpur. World Meteorological Organisation's (WMO) global station data archive on vertical atmospheric temperature profile data reported by radiosondes was used to represent atmospheric temperature inversions in June, September and December.

2.4 Statistical Calculations

Measures on descriptive statistics (mean, median, mode, standard deviation, range, percentiles) were undertaken on season-wise dataset. Student's t-test was used to estimate statistical difference in seasonal mean concentrations of TNMHC. Kruskal-Wallis One Way Analysis of Variance on Ranks test was conducted to test the medians of site-wise TNMHC concentrations over all the seasons to test significant difference amongst sites. The TNMHC concentration dataset was subjected to cluster analysis for tree clustering of sites via Ward Method. Significant differences between values were calculated by Duncan's Multiple range Test (DMRT). Statistical analyses were carried out by Statistica (Dell Software, Version 13) and MSTAT C Software (Crop and Soil Science Division, Michigan State University, USA).

3. RESULTS AND DISCUSSION

3.1 Diurnal and Seasonal Variation of TNMHC

Ground-level TNMHC concentrations had low to moderate temporal variation diurnally (coefficient of variation or CV=36–110%) as well as over post-monsoon, winter and summer seasons (CV=52–122%) apart from also having low-moderate spatial variations over the selected sites (CV=8–152%). There was also intra-site differences in TNMHC concentration amongst various chosen time periods viz. 8:00, 13:00, 18:00 and 23:00 hrs, only few of which were statistically significant (Table 2). Over the various time periods in a day (24-h), mean TNMHC concentrations ranged from 0.88–1.73 ppmV, 1.75–4.04 ppmV and 1.20–1.53 ppmV at residential sites; 2.99–6.47 ppmV, 1.52–7.38 ppmV and 0.98–1.63 ppmV at traffic site; 0.83–1.15 ppmV, 2.03–3.24 ppmV, 1.1–1.70 ppmV at residential cum commercial sites and 1.05–4.79 ppmV, 6.2–8.58 ppmV, 0.34–0.64 ppmV at purely commercial sites during post-monsoon, winter and summer, respectively. Occasional spikes in concentration (TNMHC>10 to <13.6 ppmV) were observed on three occasions at two sites on two winter days and considered in calculations, leading to high case-specific mean concentrations, but reasons thereof remained unidentified. In winter, the purely commercial site returned highest mean TNMHC values at all times of the day, followed by the traffic site. Overall, mean TNMHC values were highest in winter (mean TNMHC Conc.: 3.15 ppmV) that was >2 times higher over both post monsoon (mean TNMHC Conc.: 1.62 ppmV) and summer (mean TNMHC Conc.: 1.26 ppmV) concentrations. Weaker dispersion and ground-level subsidence of city air in winter could also have played the most significant role in causing TNMHC to scale highest values in winter. Near ground-level inversion was also prominent in winter, affecting elevated ground-level TNMHC concentrations, as discussed later in this section. Intra-season temporal variability in ground-level TNMHC concentrations was highest in post-monsoon (coefficient of variation, CV: 122%), followed by winter (CV: 80%) and summer (CV: 52%). Higher usage of biomass fuels for warming water and house warming in city slums could be one the major reasons behind highest mean TNMHC concentration in residential areas in this season. It has been estimated that about 4.9 Tg of Non-methane VOCs (NMVOCs) are generated annually in India from residential cooking (Pandey *et al.*, 2014). Fleming *et al.* (2018) have reported substantial VOC emissions from dung-fired cookstoves in Indian homes. Further, wanton open waste burning in practiced in various cities in India, leading to air pollution (Kumar *et al.*, 2018, 2015) and emissions of NMHCs (Sharma *et al.*, 2019; Chen *et al.*, 2017). In summer months, TNMHC concentrations were generally lower at all sites over all the time periods of the day which could have been influenced to a great extent by higher dispersion supported by low pressure, warmer conditions and higher wind speed (Fig. 2). Also, household fuel combustion and open waste burning towards heat generation could actually be lower in summer, leading to decline in NMHC generation. On the other hand, increasing levels of ground-level TNMHC was evident from October onwards when atmospheric temperature started to dip with approaching winter. The comparative scenario of ground-level TNMHC concentrations over the three seasons (Fig. 3) indicates some sporadic extreme and outlier values, possibly due to sampling very near to NMHC sources at ground level in congested and anthropogenically active areas. Highest mean seasonal TNMHC concentration was observed during winter due to lower dispersion followed by post-monsoon and summer. Also, the non-outlier range of TNMHC concentration was highest in winter. Summer had no outliers and range of TNMHC concentrations was low, probably due to apparent lack of commercial roadside cooking in summer when dining out declines and also, declining open burning activities for lack of need of warmth,

Table. 2. A summary of average TNMHC concentrations (ppm) at different times of day and sites over various seasons.

Time	Post-Monsoon				Winter				Summer			
	Residential	Traffic	Residential +commercial	Pure commercial	Residential	Traffic	Residential +commercial	Pure commercial	Residential	Traffic	Residential +commercial	Pure commercial
08:00	0.88 a	2.99 a	1.15 a	1.20 a	2.17 a	1.52 a	2.04 a	8.58 a	1.53 a	1.60 a	1.54 a	0.64 a
13:00	0.92 a	6.47 b	0.88 a	4.79 b	1.75 a	1.89 a	2.07 a	6.72 a	1.27 a	0.98 a	1.68 a	0.53 a
18:00	1.73 a	4.90 ab	1.08 a	1.05 a	4.04 a	7.38 b	3.24 a	6.81 a	1.21 a	1.14 a	1.15 a	0.34 a
23:00	1.34 a	5.06 b	0.83 a	4.04 ab	2.75 a	4.08 a	2.03 a	6.20 a	1.20 a	1.63 a	1.70 a	0.49 a

Values followed by same letters are not statistically different from each other at 5% level of significance as per DMRT.

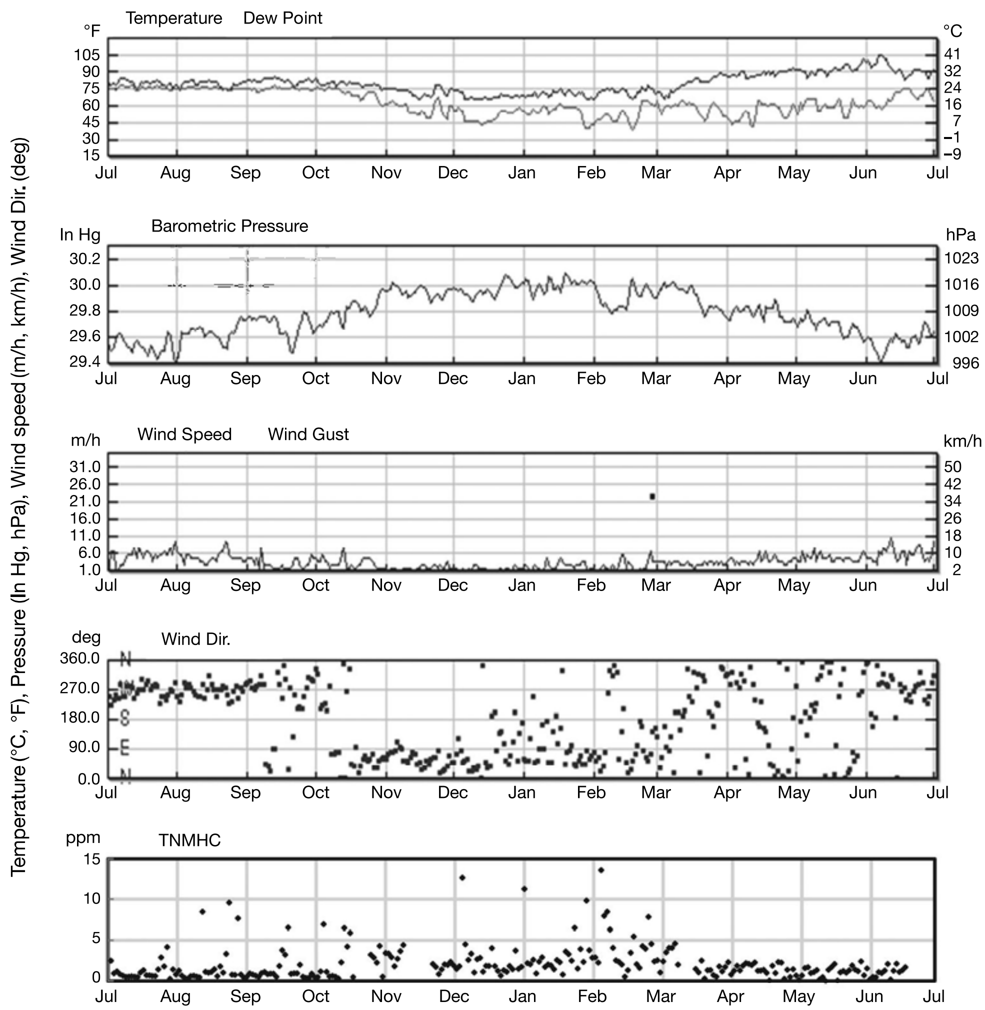

Fig. 2. Seasonal variation in atmospheric temperature, dew point temperature, barometric pressure, wind speed and gust, and wind direction in Nagpur city during the study.

accompanied by quick dispersal after generation.

All-season data in terms of daily time-dependent TNMHC concentrations reflected that concentrations at 8:00 and 23:00 h were frequently lower than 13:00 and 18:00 h (Fig. 4). Higher TNMHC concentrations at 13:00 and 18:00 h could be strongly influenced by *real time* vehicular movements and commercial activities that remain at their peaks during these hours in Nagpur. At Itwari (purely commercial site), a winter day witnessed a bout of relatively higher TNMHC concentrations, ranging from 7.8–12.6 ppmV while another winter day witnessed a concentration of 13.6 ppmV at 18:00 h in Mahal (a residential site). In terms of season-wise mean TNMHC concentrations, highest was observed during winter due to potentially lower dispersion of ground-lev-

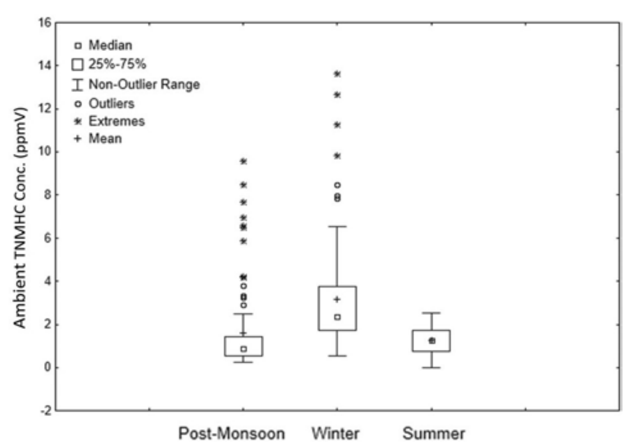

Fig. 3. Summary statistics of near-ground TNMHC concentrations in different seasons.

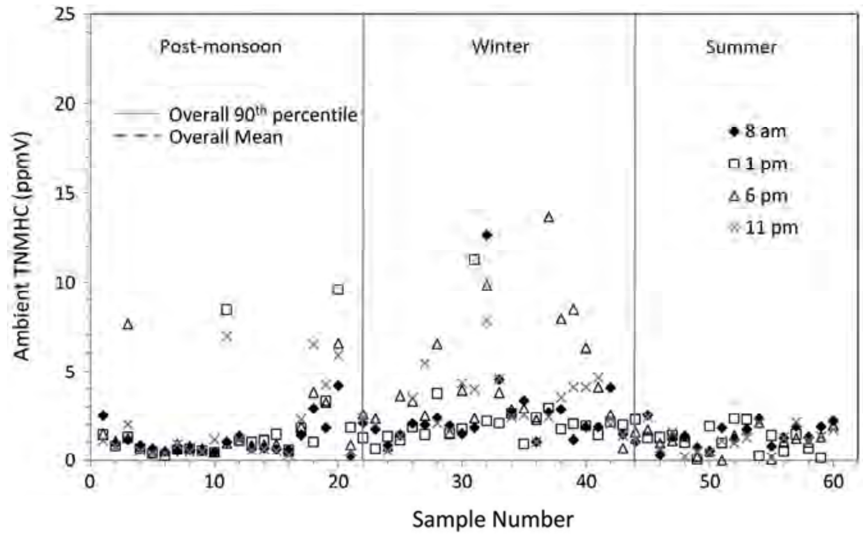

Fig. 4. Distribution of near-ground TNMHC concentrations over Nagpur city *vis a vis* different times of a day over all the selected seasons (post-monsoon, winter and summer).

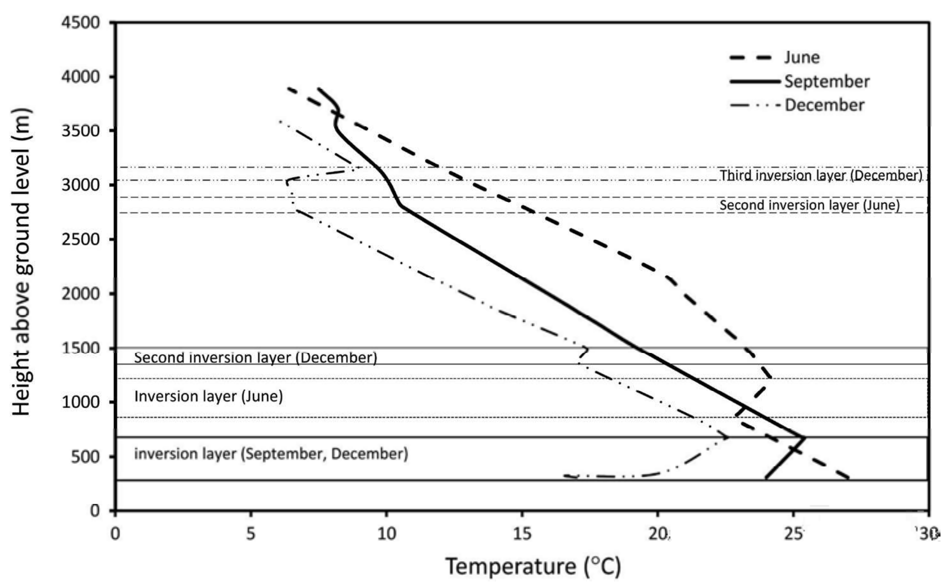

Fig. 5. Vertical temperature profile and inversion layers over Nagpur city in June, September and December months during the study.

el air, followed by post monsoon while summer concentrations were persistently the lowest. There was a presence of strong ground-level inversion in winter (in December) (approx <250–750 m) revealed by Radiosonde data on vertical atmospheric temperature profile over Nagpur (Fig. 5), signifying increased chances of lower dispersion of pollutants at ground level. Also, a weaker inversion was observed in September (post-monsoon season), just before the winter set in. However, during peak summer of June, near-ground inversion was absent and the inversion layer was detected above 750 m height above ground, indicating better chances of dispersion and dilution of air pollutants at ground level. Descriptive statistics of a season-wise database is presented in Table 3, which reflects stand-alone characteristics of winter TNMHC concentrations. The season-wise TNMHC database were found to be normally distributed.

TNMHC concentrations at some locations measured during Diwali Festival (Festival of Lights which is characterized by large-scale firecrackers bursting and coinciding with late post-monsoon season), ground-level TNMHC concentrations hovered mostly around 3–4.4 ppmV, which almost matched with 90th percentile of post-monsoon concentrations excepting Diwali period. Although concentrations >4 ppm were obtained on 2 different occasions on Diwali day that were more than average summer concentration and also, post-monsoon concentrations on several days, no persistent increasing or decreasing trend in ground-level concentrations were observed over pre- or post-Diwali periods. Emissions from firecracker bursting is reportedly instrumental in elevating ambient concentrations of NMHCs (Chang *et al.,* 2011).

Table 3. Outcome of Descriptive statistical test on air quality data.

Parameter	Post-Monsoon	Winter	Summer
Sample number	83	84	72
Mean (ppm TNMHC)	1.61	3.15	1.26
Median (ppm TNMHC)	0.88	2.38	1.28
1st quartile (ppm TNMHC)	0.56	1.76	0.78
3rd quartile (ppm TNMHC)	1.44	3.75	1.72
Geometric mean (ppm TNMHC)	1.04	2.52	0.94
Interquartile range (ppm TNMHC)	0.88	1.99	0.94
Variance (ppm TNMHC)	3.91	6.42	4.34
Skewness	2.44	2.34	$-9.56*10^{-2}$
Kurtosis	5.46	5.94	$-7.18*10^{-1}$
Distribution (Anderson-Darling normality test)	Normal	Normal	Normal

3.2 Site-Specific Variability in Ground-level TNMHC

Site-specific TNMHC concentrations over all the seasons together (Fig. 6) revealed important observations in terms of influence of site-specific activities on ground-level TNMHC concentrations. Mean TNMHC concentrations were found to be highest at the commercial site (Itwari), closely followed by a residential cum commercial site (Wanadongri). While Itwari is known to have strong NMHC sources like vehicles, commercial cooking, petrol pumps and DG sets, the residential cum commercial areas also had some of the similar sources apart from various household ones. On the other hand, the traffic site had lower TNMHC concentrations than several primarily residential areas rather unexpectedly. But, it was noted that roadside eateries and biomass combustion activities were co-existent with other activities in many residential areas in this UA, making the latter potentially a strong TNMHC emission hub. Guo *et al.* (2004) reported that internal combustion engines, unburnt fuel, solvents including paints, liquefied petroleum gas (LPG) or natural gas leakages, solvents, fuel

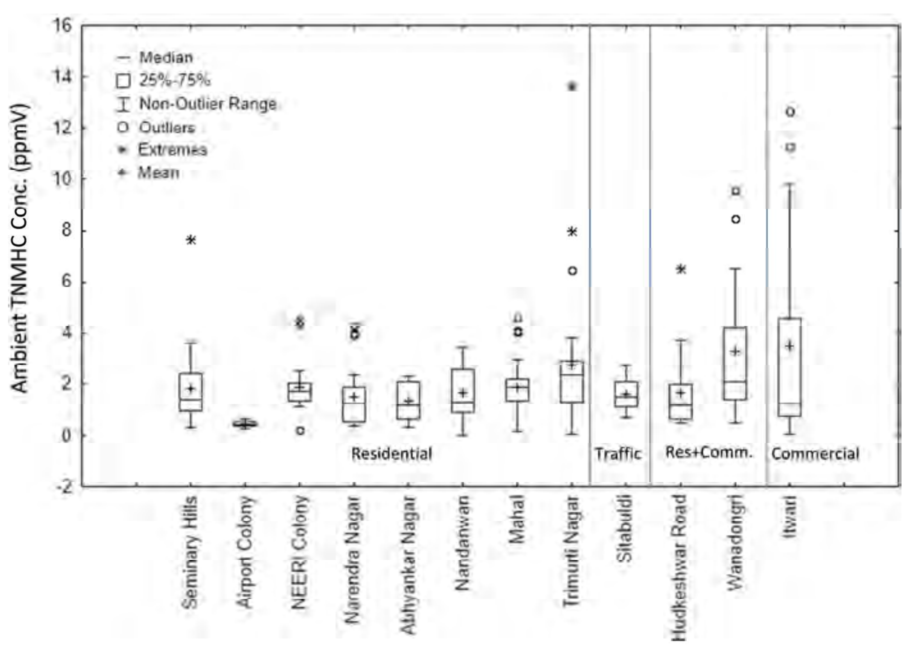

Fig. 6. Site-wise summary statistics of ambient TNMHC concentrations recorded over post-monsoon, winter and summer.

combustion, chemical factories and power plants were the major sources of NMHCs in Hong Kong. In Nagpur, a few of above sources could potentially get together to contribute to TNMHC present in ground-level air and might be one of the reasons for getting sporadic high concentrations in residential areas. As per Kruskal-Wallis One Way Analysis of Variance on Ranks test, the differences in the median values among the sites, in terms of TNMHC concentrations over all the seasons together, are greater than would be expected by chance and therefore, there was a statistically significant difference ($P \leq 0.001$).

Cluster analysis was performed and the branching dendrogram represented similarity or dissimilarity amongst various groups of sites in terms of ground-level TNMHC concentrations (Fig. 7). The site-groups of Airport Colony and Narendra Nagar; Nandanwan and Wanadongri were categorized as similar ones and were not very different from each other. The sites of Sitabuldi, Itwari and Seminary Hills, Mahal were outstanding in nature and were also much different from others, as revealed by height of their vertical lines that signified the degree of difference between branches i.e. longer the line, greater is the difference. Seminary Hills, Hudkeshwar and NEERI Colony could also be categorized as stand-alone sites in terms of ground-level TNMHC concentrations.

Ambient TNMHC concentrations reported by various researchers over the world are observed to be highly variable spatially and temporally. Zielinska *et al.* (2001) in a study conducted near California/Mexico border reported concentration ranges of <0.1 ppm to slightly greater than 0.2 ppm at Rosarito at 10:00 AM and 1:00 PM samples while another site Mexicali showed concentrations up to near about 2.4 ppm in 6:00 AM samples in the month of September. As per Nishanth *et al.* (2014), the annual maximum, minimum and average TNMHCs were 25.45, 13.84 and 19.23 ppbv, respectively, in a rural coastal location at Kannur, India during November 2009 to December 2011. Chen *et al.* (2014) reported TNMHC concentration distribution over 2007–2011 in Taiwan under two monitoring networks viz. air quality stations (AQS) of USEPA across Taiwan and Photochemical Assessment Monitoring Stations (PAMS) that generate hourly observations of 56 non-methane hydrocarbons (NMHCs). The time-series concentrations by both networks showed wide temporal variations but maximum TNMHC values reached were about 1.6 ppm under both networks while the lowest concentrations touched down to about 0.02 ppm in PAMS. Sharma *et al.* (2016) measured TNMHC at one site during the month of May in New Delhi, India and reported that TNHMC concentration varied from 0.22–0.25 ppm during day to night time. The low variation in this study obviously was a result of short duration of study and also, summer being chosen as the study time, when ground-level air is known to have good all-round dispersion and vertical mixing as well. In a study conducted in summer season at three locations in a zone of 5 km radius around Mathura Refinery in India, TNMHC was found in the range of 0.11–5.7 ppm while at two of the sites, concentration was frequently found

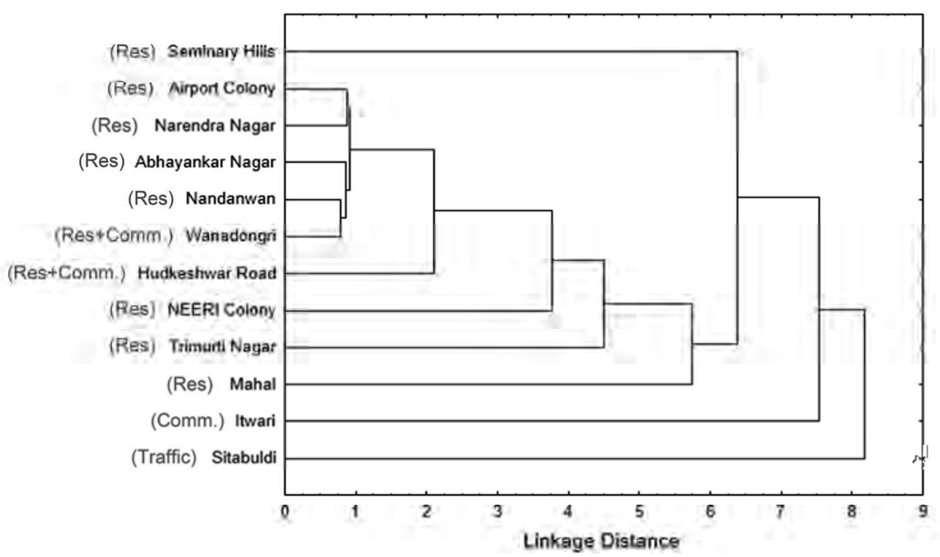

Fig. 7. Cluster pattern of selected sites in terms of ambient TNMHC mixing ratio recorded over all the seasons.

over 4 ppm and 2 ppm during the short study (EIL, 2015). Vehicular traffic emissions were found to be one of the predominant sources of hydrocarbons at these stations.

Considering year-round average (2.02 ppmV), 90th percentile (4.07 ppmV), several instances of high TNMHC concentrations in short-period samples of this study and also, in the light of average TNMHC concentrations reported at some other locations in the world, it is evident that a good number of short-term TNMHC concentrations encountered in this study were much higher than reported in most other studies. The reasons thereof could be: this study reports ground-level concentrations at the height of only about 1.5 m, which at times were directly sampled (i) near kerb sites severely affected by traffic emissions or nearby commercial activities like burning fossil fuels like biomass, charcoal, coal and LPG in closely located restaurants and mobile food vendors or (ii) just adjacent to streams of city crowd where influence of environmental tobacco smoke on TNMHC concentrations cannot be ruled out or (iii) within the influence zones of petrol pumps that are abundant and quite close to each other in this city. Even ground-level sampling in residential zones could be influenced by occasional traffic movements, especially of two-wheelers that are popular in this city.

3.3 Weekday-Weekend Variability in Ground-level TNMHC

There was subtle weekend effect on mean ground-level TNMHC concentrations observed over all sites, time-periods and the seasons. A few of the higher TNMHC concentrations were recorded during winter weekdays while mean TNMHC concentrations on weekends (Sundays) in all the seasons were lower than weekdays. It may be noted from mean and 90th percentile values of TNMHC reported in Fig. 8 that the escalations registered in mean TNMHC concentrations on weekdays over weekends were low and statistically insignificant (1.17–1.21 times more on weekdays) but perceptible in all seasons. This probably hinted at a slim positive influence of larger on road vehicular fleet and escalated commercial activities of weekdays on ground-level NMHCs. Traffic-driven TNMHC emissions have been aptly reflected in the study of Liu *et al.* (2014), where TNMHC concentrations within a traffic tunnel was found to reach up to about 2.8 ppm when the traffic was slow-moving at about 45 km h^{-1}, which is similar to general traffic movement speed in most Indian cities. In another tunnel study in Taiwan (Chang *et al.*, 2008), where downslope entrance, downslope exit, upslope entrance and upslope exits were monitored, average TNMHC was observed to be 1.9, 3.5, 0.8 and 2.7 ppm.

4. CONCLUSIONS

Intra-season variability in ground level TNMHC in Nagpur were low to moderate. Concentrations in winter

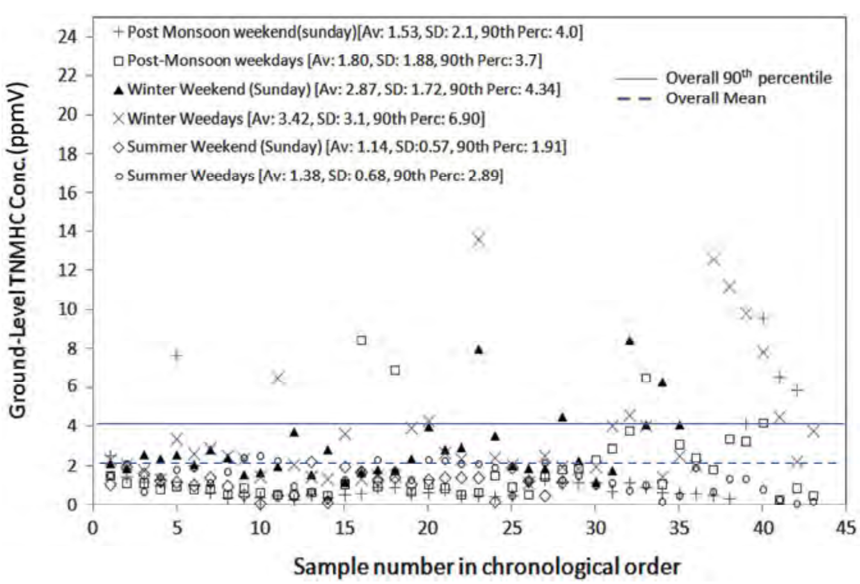

Fig. 8. Distribution and summary statistics of TNMHC concentrations during weekdays and weekends in different seasons.

were conspicuously higher over other seasons and concentrations in summer were lowest, evidently due to better dispersion. In spite of lower dispersion with dipping night-time temperature, TNMHC build-up was not found to be alarming at 23:00 h over day-time hours in any season and observed concentrations at 23:00 h were almost consistently lower than noon and evening-time concentrations when higher vehicle movements and operation of other sources might have played a major role in elevating ground-level TNMHC. At morning 8:00 h when atmospheric temperature remains lower than noon and evening, there was no substantial build-up of TNMHC, probably because winter is mild in Nagpur and by morning 8 o'clock, the city heats up substantially to allow good dispersion. Causes of spurts in ground-level TNMHC at some localities could not be identified.

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