

Emissions and atmospheric concentrations of monoterpenes in a semi-arid region of India: Role of winter to summer changes in meteorological conditions

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Abstract

Emissions of biogenic volatile organic compounds (BVOCs) play important roles in ecophysiology and atmospheric chemistry at large spatial and temporal scales. Tropical regions are a main global source of BVOCs and magnitude and chemical compositions are highly variable. This study is based on the measurement of monoterpenes using a proton transfer reaction-time of flight-mass spectrometer (PTR-TOF-MS) at a semi-arid site in western India during winter-to-summer transition period of February-March 2014. Mixing ratio of monoterpenes showed strong diurnal variation with elevated values from evening till midnight and lowest in the afternoon. The daytime mixing ratio increased from 0.19 ppbv in first half of February to 0.40 ppbv in second half of March. Both the nighttime and daytime ratios of monoterpenes/benzene in second half of March were 2-3 times higher their values during first half of February. In March, it showed strong response with temperature during both day and night and increased from about 0.27 ppbv ppbv⁻¹ at lower temperatures to >0.50 ppbv ppbv⁻¹ at higher temperatures. The dependence with wind speed showed exponential decay but the rate of decline in February was ~2 times greater than that in March. The nighttime ratios of monoterpenes/isoprene were significantly higher than those in the daytime indicating light independent but temperature dependent emissions of monoterpenes. The ratios of monoterpenes/isoprene agree with the values reported for a topical forest region in SE Asia. The estimated 36% increase in monoterpene emissions from winter to summer conditions is due to the increase of biogenic emissions. The NW winds and higher ambient

25 temperatures in March favored the local emissions and regional transport of BVOCs. Exceptionally high levels of 3-6 ppbv were measured during the sporadic biomass burning and bonfire events particularly during the *Holi* festival.

Keywords: Monoterpenes; Biogenic emissions; Biomass burning, BVOCs, Winter-Summer Transition, Tropical Asia, India

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1. Introduction

In the atmosphere, photo-oxidation reactions of volatile organic compounds (VOCs) and oxides of nitrogen ($\text{NO}_x = \text{NO} + \text{NO}_2$) lead to the production ozone (O_3) (Liu et al., 2008). Secondary organic aerosol (SOA) is produced from gas-to-particle conversion processes of VOCs and their oxidation products (Jimenez et al., 2009). Elevated levels of VOCs can suppress the concentration of hydroxyl (OH) radical and enhance the formation of peroxy (HO_2 and RO_2) radicals and organic nitrates such as peroxyacetyl nitrate (PAN) (Stewart et al., 2003). Globally, VOCs are emitted from various anthropogenic and natural sources. The terrestrial vegetations emit large quantities of biogenic volatile organic compounds (BVOCs) including reactive non-methane hydrocarbons (NMHCs) and oxygenated-VOCs (OVOCs). Terpenoids such as isoprene (C_5H_8), monoterpenes ($\text{C}_{10}\text{H}_{16}$, MTs) and sesquiterpenes ($\text{C}_{15}\text{H}_{24}$) are the primary constituents of BVOCs. Among several monoterpenes, α - and β -pinenes are the most dominant species in ambient air (Jardine et al., 2015). Monoterpenes are highly reactive species and have large and varying effects on regional atmospheric chemistry (Hallquist et al., 2009). Monoterpenes have a short atmospheric lifetime ranging from several minutes to hours due to rapid reactions with OH, O_3 and nitrate (NO_3) (Atkinson and Arey, 2003). Many plants emit BVOCs due to normal metabolism and stress metabolism (Fall, 1999; Peñuelas and Staudt, 2010). The emission flux of BVOCs from plants depends on environmental condition (Calfapietra et al., 2013; Loreto and Schnitzler, 2010). Generally, the emission rates of BVOCs are dependent upon solar radiation, temperature, relative humidity (RH) which can lead to substantial diurnal variability (Kesselmeier and Staudt, 1999;

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50 **Portillo-Estrada et al., 2018** . In plants, storage structures such as the resin duct and the glandular cells lead to pool emissions and account for both the daytime and nighttime release of terpenes. The emission of terpenes from recently assimilated carbon and which is tightly coupled with photosynthesis and metabolism is another important pathway (Wu et al., 2017). Emission rates of monoterpenes are also influenced by age of leaf and tree (Thoss et al., 2007) water and nutrient availability (Blanch et al., 55 2009) and seasonality (Hakola et al., 2006).

Global emission fluxes of BVOCs are estimated to be ~7 times greater than those of **anthropogenic VOCs** (Stewart et al., 2003). The annual global emissions of BVOCs have been estimated to be about 1150 TgC yr⁻¹ comprising about 44% of isoprene and 11% of monoterpenes (Guenther et al., 1995, 2012; Sindelarova et al., 2014). The emissions from tropical region contribute about 80-85% to the 60 global budgets of isoprene and monoterpenes (Sindelarova et al., 2014). But there are considerable uncertainties in global emission estimates due to the large number of BVOC species and a variety of biological sources (Guenther, 2013). **In the literature, a wide range of emission estimates for monoterpenes are mainly due to the lack of observational data and poor understanding of emission mechanism (Arneeth et al., 2008)**. Much of the recent works on emission and atmospheric chemistry of 65 BVOCs have been focused on isoprene. Emission rates of monoterpenes are estimated to be small compared to isoprene but it can have a disproportionate effect on aerosol formation due to higher SOA yields (Griffin et al., 1999).

In the tropics, sparse measurements of BVOCs cause higher uncertainties in their emission estimates and atmospheric importance. Although there has been significant growth of literature available about 70 tropical BVOC emission in Amazonia and in tropical Africa, but there is still a paucity of data on BVOC emission in tropical Asia (Wang et al., 2007; Sahu, 2012). The measurements of BVOC emission rates from tropical plants are limited and are particularly lacking over the Indian subcontinent (Varshney and Singh, 2003). **Biogenic emissions have been reported to make a significant contribution to total VOC in many cities of the world (Calfapietra et al., 2013 and references therein). Sarkar et al. (2016) have 75 reported the measurements of various VOCs using a proton transfer reaction time of flight mass**

spectrometer (PTR-TOF-MS) instrument in the Kathmandu Valley, Nepal during the winter of 2012-2013. Nonetheless, accurate and time resolved measurements of BVOCs are important to study the chemical compositions of the tropical troposphere. The present study is based on analysis of ambient mixing ratio data of monoterpenes measured using PTR-TOF-MS 8000 instrument at an urban site of Ahmedabad in western India during February-March 2014. The objective of this study is to investigate the contribution of different sources and trends of biogenic emissions of monoterpenes in the context of the change in meteorological parameters during winter-to-summer transition.

2. Measurement site and PTR-TOF-MS instrumentation

The measurement site (23.0356° N; 72.5435° E, 49 m above sea level) is located in the campus of Physical Research Laboratory (PRL) in Ahmedabad city. It is the largest city in the state (province) of Gujarat with a population of more than 6.3 million and area of about 466 km². The *Sabarmati* river divides the city into eastern and western parts. As shown in Fig. 1, the study site is located in the western part of the city where vehicle exhaust is a major source of air pollution including anthropogenic VOCs (Sahu et al., 2016a). According to latest data, about 3.2 million vehicles are registered in Ahmedabad which is increasing at a rate of about 10% yr⁻¹ (Chandra et al., 2016). The eastern part has several industrial estates especially of textiles, chemicals, plastics, metal alloys, machinery, etc. As shown in Fig. 1, the inner and outer roads encircling the city are the 132 feet ring road and Sardar Patel (SP) ring road, respectively. Therefore, irrespective of wind direction, emissions from vehicle exhaust are expected to be the dominant source of AVOCs in the city. Except sporadic local biomass burning events, use of biomass burning in this one of the most economically and technologically developed regions of India is small compared to Indo-Gangentic Plains (IGP) where activities of biomass burning are rampant in winter. The trees cover about 6% of total area in Ahmedabad city. About 6.18×10⁵ trees were counted in the year 2011 with relatively higher coverage in the western and south parts than those in eastern and north parts. As shown in Fig. 1, the major plant species found in the city are *Azadirachta indica*, *Polyalthia longifolia* and *Holoptelea integrifolia* and *Delonix regia* (Limbochiya and Patel,

2013). The significant emissions of monoterpenes from the major plant such as *Azadirachta indica* and *Delonix regia* are reported in forested areas of *Haryana* state and Delhi in India (Padhy and Varshney, 2005; Singh et al., 2011). In India, emissions of isoprene from common plant species have been examined to some extent (Singh et al., 2011; Varshney and Singh, 2003). As shown in Figure 1, tree species such as *Mangifera indica*, *Eucalyptus globulus*, *Ficus benghalensis*, *Syzygium*, etc. are significant α -pinene emitters for which emissions of isoprene were reported (e.g., Padhy and Varshney, 2005; Varshney and Singh, 2003 and references therein). The surrounding areas of the city are mostly agricultural land with a lower tree cover of about 4.75% of the total geographical area. The *Thol* wildlife sanctuary with a total area of 700 ha is situated at a distance of about 25 km northwest (NW) of Ahmedabad city. The vegetations found in the *Thol* sanctuary are mainly scrub type with mixed flora of aquatic and marshy plants (Vyas, 2014). Gandhinagar, also known as India's tree capital which has a green cover of about 54%, is located approximately 23 km north of Ahmedabad city. Therefore, relatively higher levels of BVOCs are expected during February-March period when NW winds prevail.

Real-time continuous measurements of ambient VOCs were made using the PTR-TOF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) during 01 February-31 March 2014. The PTR-TOF-MS 8000 instrument provides very fast, sensitive and high mass resolution measurements of various VOC compounds present in the air. The drift tube pressure of ~ 2.3 mbar, the drift tube temperature of 60 °C and the drift tube voltage of 660 V were maintained throughout the study period. This drift tube setup corresponds to an E/N ratio of 128-130 Townsend (Td) ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$), where E is electric field and N is number gas density. The typical E/N ratios of 120-140 Td is recommended for ground level ambient measurements using the PTR-MS (Hewitt et al., 2003). Ambient air flow rate of 60 mL min^{-1} through a 1.5 m long heated (60 °C) Teflon® PFA tube (1/8" or 3.175 mm) was maintained during the study period. The raw data files in 'hdf5' format were acquired using the TOF-Daq software (version 1.2.93, Tofwerk AG, Switzerland). Subsequently, the "PTR-TOF Data Analyzer" software was used for further processing of the data (Müller et al., 2013). Since the reagent ions ($\text{H}_3^{16}\text{O}^+$; at m/z 19.0178) may saturate the multi channel plate (MCP) detector, we calculated the rate count of $\text{H}_3^{16}\text{O}^+$ from $\text{H}_3^{18}\text{O}^+$ (at m/z 21.0221) signal by assuming a natural abundance ratio of $^{16}\text{O}/^{18}\text{O}$ (499:1). In this

paper, we have presented the mixing ratio data of monoterpenes (MTs) measured at m/z 137.131 (C₁₀H₁₆-H⁺) and by taking account of its product at m/z 81.07 (C₆H₈-H⁺). A certified gas mixture containing 0.97 ppmv \pm 5% of α -pinene (L5388, Ionicon Analytik GmbH Innsbruck) was used for the calibration and determination of sensitivity. The responses of m/z 137.131 and its product were calibrated using a standard mixture containing only one monoterpene (α -pinene) among other VOCs. Therefore, in the calibration, the detected fragmentation at m/z 81.07 was only due to α -pinene and does not represent contributions or interferences of other monoterpenes. The measurement precision of 2.7% was determined using 20 min time series of 30s time resolution data at a constant value of about 3 ppbv. The background level (zero) is important for the determination of the sensitivity of the PTR-TOF-MS. Therefore, instead of direct supply of ambient air with variable VOC level as input in the gas calibration unit (GCU) (GCU-advanced v2.0, Ionicon Analytik GmbH, Austria), the high quality and stable production of VOC-free zero air was obtained by connecting ultra purity (99.9999%) zero air generator (Parker HPZA-3500-220) in tandem with the GCU (see supplementary information Fig. S1). The overall accuracy of monoterpene data is estimated to be about less than 10% which is mainly due to the uncertainties of the standard mixture and set flow rates of both the gases in the GCU. Further details of calibration procedure, determination of sensitivity and transmission efficiency are given in supplementary information (Fig. S2, Fig. S3). The mixing ratios of other VOCs such as benzene(C₆H₆), isoprene (C₅H₈), acetonitrile (CH₃CN) were used as supporting data already reported in our previous paper (Sahu et al., 2017). The measurement details of isoprene and benzene are reported in our previous publications (Sahu et al., 2015, Sahu et al., 2016b).

3. Results and discussion

3.1 Time series of monoterpenes and meteorological parameters

Hourly and daily time series of monoterpenes show large variations during the study period (Fig. 2). In February, hourly average mixing ratios varied in the range of 0.05-3.5 ppbv, while daily averages were in the range of 0.11-0.92 ppbv. The monthly average mixing ratio of monoterpenes in February was

0.37±0.2 ppbv. In short time scales (<24 h), large periodic variations indicate strong diurnal dependence
155 of monoterpenes, while day-to-day variations seem to be controlled by the synoptic-scale weather
conditions. Time series of wind speed, temperature, pressure and solar flux and planetary boundary layer
(PBL) depth are also plotted in Fig. 2. Typically, the periods of low and high mixing ratios coincide with
the episodes of strong and weak winds, respectively. For example, daily mean values exceeding 0.5
ppbv during 2-5 February and 18-20 February coincided with light winds and warmer weather
160 conditions with daily maximum temperature exceeding 30°C. On the other hand, periods of low
monoterpenes (<0.2 ppbv on daily scale) during 10-13 February and 23-24 February were influenced by
relatively strong winds and lower surface temperatures. The actual concentration depends on the
emission flux, oxidation and vertical mixing (Mielke et al., 2010). Therefore, signatures of biogenic
emissions in the mixing ratio data are obscured due to dominating influence of vertical mixing and
165 oxidation loss processes. However, to some extent, the ratio of monoterpenes to benzene (an
anthropogenic tracer) can take account of variations due to change in local meteorology and PBL.
Hourly monoterpenes/benzene (MTs/benzene) ratio exhibits large periodic variation which tends to
follow the diurnal cycle of temperature. It showed slightly increasing trend with average ratios of
0.19±0.03 and 0.26±0.07 ppbv ppbv⁻¹ during the first and second halves of February, respectively.

170 Time series of monoterpenes in March also showed significant hourly and day-to-day variations. The
amplitudes of hourly data during the first half of March were larger than those observed during the
second half of March. In this month, hourly and daily mean mixing ratios of monoterpenes varied in the
ranges of 0.06-6.1 ppbv and 0.09-1.12 ppbv, respectively. The monthly average mixing ratio of
monoterpenes was 0.35±0.3 ppbv in March. The periods of elevated monoterpenes, for example during
175 15-17 March, coincided with calm winds and warmer temperatures. Daily averages of MTs/benzene
ratio were in the range of 0.11-1.68 ppbv ppbv⁻¹ during March. Most significantly, the ratios increased
from 0.20±0.07 ppbv ppbv⁻¹ in the first half of February to 0.50±0.40 ppbv ppbv⁻¹ in the second half of
March. The monthly average of MTs/benzene ratio in March (0.36±0.16 ppbv ppbv⁻¹) is significantly
higher than that in February (0.22±0.06 ppbv ppbv⁻¹). This trend in MTs/benzene ratio is consistent with
180 that of daily mean temperature which increased from 17-25 °C in February to 20-30 °C in March. The

day and night statistics of monoterpenes, acetonitrile (a biomass marker), MTs/benzene ratio, and meteorological parameters for the first half of February and second half of March are presented in Table 1. The statistics presented in Table 1 are excluded for the measurements during two major anthropogenic events which are described in following section. The mean mixing ratios of monoterpenes in rural New Hampshire, USA were 0.50 ppbv in the summer season and 0.10 ppbv in the winter season (Haase et al., 2011). The monthly daytime and nocturnal average mixing ratios of at New Hampshire were ~0.6 and 1.6 ppbv, respectively. At a site in Montseny, NE Spain, levels of monoterpenes were 2.56 ppbv and 0.23 ppbv during the summer and winter seasons, respectively (Seco et al., 2011).

3.2 Impact of biomass burning

The major anthropogenic sources of monoterpenes are wood processing in sawmill, biomass burning burning and traffic (Hellén et al., 2012; Koss et al., 2018; Schade and Goldstein, 2003). Several studies have reported that the massive amounts of BVOCs can be emitted in response to burning vegetation and wounding at high temperatures (Loreto and Schnitzler, 2010; Müller et al., 2016). Among different BVOCs, emission of α -pinene has been found as a major monoterpene in fresh biomass burning plumes (Akagi et al., 2013). The mixing ratio of acetonitrile is commonly used as a marker to track biomass burning plumes (Holzinger et al., 1999). The time series of MTs, acetonitrile and benzene, and MTs-acetonitrile correlation plots during two major events of biomass burning are shown in Fig. 3. In the first episode, from the evening of 19 February until the morning of 20 February, the mixing ratios of monoterpenes and acetonitrile show large simultaneous enhancements with their peak values exceeding 3 ppbv (Fig. 3a). The strong correlation ($r^2 = 0.91$) and a high $\Delta\text{MTs}/\Delta\text{CH}_3\text{CN}$ slope value of 1.08 ppbv ppbv⁻¹ indicate strong impact of fresh biomass burning emissions (Fig. 3b). In Fig. 3 c and d, variation of monoterpenes and acetonitrile are shown for another major event of biomass burning from the evening of 15 March until early morning of 16 February coincide with *Holi* festival bonfire in India. *Holi* is a spring festival in India which is celebrated in the month of *Phalgun* according to the Indian Calendar or in the months of February/March. Traditionally, huge bonfires are lit on the night preceding

Holi festival and the event is known as ‘*Holika Dahan*’. Therefore, huge amounts of semi-dry biomass and wood burned across the Indian subcontinent could contribute to the emission of many trace gases including BVOCs. During *Holika Dahan*, the mixing ratios of monoterpenes and acetonitrile show large and correlated enhancements with their peak values exceeding 6 ppbv and 4 ppbv, respectively (Fig. 3c). The strong correlation ($r^2 = 0.89$) and a high $\Delta\text{MTs}/\Delta\text{CH}_3\text{CN}$ slope value of $1.46 \text{ ppbv ppbv}^{-1}$ indicate strong impact of the *Holi* bonfire (Fig. 3d). For the rest of the measurement period, the nighttime $\Delta\text{MTs}/\Delta\text{CH}_3\text{CN}$ slopes of $\sim 0.5 \text{ ppbv ppbv}^{-1}$ were determined separately for February and March months. These lower nighttime $\Delta\text{MTs}/\Delta\text{CH}_3\text{CN}$ slopes clearly highlights that the most of the data were not directly influenced by the biomass burning plumes.

Except sporadic biomass burning events (e.g., *Holi*), the mixing ratios of monoterpenes measured during different periods do not show any clear dependence on benzene and acetonitrile. Therefore, the mixing ratio of both benzene and acetonitrile serve as good references for delineation of anthropogenic sources. In this study, ratio of MTs/benzene has been considered to take account of the variations due to anthropogenic emissions and PBL dynamics. The scatter plots of monoterpenes mixing ratio and MTs/benzene ratio with acetonitrile are shown in Fig. 4. For each month, the data points show clear segregation depending on the local time (LT). In the daytime, most of the data points with elevated MTs/benzene ratios were measured at lower acetonitrile concentrations ($< 1 \text{ ppbv}$). For lower acetonitrile concentrations, the ratios increased from $\sim 0.24 \text{ ppbv ppbv}^{-1}$ in February to $0.40 \text{ ppbv ppbv}^{-1}$ in March. But for higher acetonitrile values ($> 1 \text{ ppbv}$), the lower ratios of $\sim 0.18 \text{ ppbv ppbv}^{-1}$ were measured during both the months. In March, the large number of data points with elevated MTs/benzene ratios compared to those in February indicates higher contributions from biogenic sources. Clearly, the increasing trend of MTs/benzene ratios during winter-summer transition is not associated with anthropogenic or biomass burning sources and mainly governed by the biogenic sources.

3.3 Diurnal profiles of monoterpenes and MTs/benzene ratio

Average diurnal mixing ratio profiles of monoterpenes for four different periods of 1-15 February, 16-28 February, 1-15 March and 16-31 March are plotted in Fig. 5a. Mixing ratio of monoterpenes showed

strong diurnal dependence throughout the study period. Except for the afternoon hours, mixing ratios of monoterpenes showed significant differences between the first and second halves of February. From night till early morning hours, mixing ratios of monoterpenes observed in the second half of February were about 2 times higher than those in the first half. Mixing ratios were moderate from midnight till the noon (00-12 h) and decreased to the lowest values in the afternoon (12-17 h). The afternoon values increased slightly from 0.11 ± 0.02 ppbv in the first half of February to 0.16 ± 0.01 ppbv in the second half of March. From evening till midnight (18-24 h), mixing ratios (0.20-0.75 ppbv) were elevated but exhibit significant differences between the four different periods. **The higher nighttime mixing ratios of monoterpenes measured during 16-28 February compared to 15-31 March do not necessarily reflect the higher biogenic contributions for the former period. As shown in Fig. 2, the lower PBL heights associated with stronger temperature inversions could be an important factor, leading to higher nighttime mixing ratios of monoterpenes during 16-28 February. As explained later in this section, the nighttime MTs/benzene ratio shows just opposite trend with higher values for 15-31 March compared to 16-28 February.** The summer season diurnal pattern of monoterpenes in Montseny (Spain) showed higher daytime values of ~ 1.6 ppbv and lower night values of ~ 0.2 ppbv (Seco et al., 2011). Warneke et al., (2004) report that the highest mixing ratios of 0.34 ppbv during nighttime and lowest at midday (0.02 ppbv) at New England in summer season.

Several local factors such as emission, photo-oxidation and PBL processes play important role in controlling the diurnal dependence of monoterpenes. Biogenic emissions of monoterpenes occur throughout the day and night but their strong diurnal dependence indicates buildup in the shallower nighttime boundary layer (Kaser et al., 2013). The combined effect of growing PBL depth and reactivity with O_3 and OH leads to depletion during daytime (Hakola et al., 2012). **Therefore, biogenic emissions during the daytime seem insufficient to counter the effects of removal due to dynamical and chemical processes in the lower troposphere.** Although ratio of MTs/benzene may take account of the variations caused by local meteorology and PBL dynamics but photochemical reaction rates of monoterpenes ($6.08-7.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and benzene ($1.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) with OH differ significantly (Atkinson and Arey, 2003; Chuong et al., 2002). Therefore, the ratio of MTs/benzene does

260 not fully take account of photochemical loss but underestimates the enhancement caused by biogenic emissions in the daytime. Consequently, the daytime enhancements of MTs/benzene ratio described in the present study could be even higher. Nonetheless, the purpose of this study is to demonstrate the relative change in biogenic emissions due to change in environmental parameters associated with winter-to-summer transition.

265 Average diurnal profiles of MTs/benzene ratio can be described as bimodal with peaks in the early morning and afternoon hours (Fig. 5b). Although the ratio showed similar diurnal patterns during different periods but the levels increased rapidly from winter to summer. The lowest values were observed from evening till midnight during each of four periods. While elevated ratios were observed in the afternoon hours (13-18 h) with peak at around 16 h. In the afternoon, the ratio increased from 270 0.17 ± 0.03 ppbv ppbv⁻¹ in the first half of February to 0.43 ± 0.07 ppbv ppbv⁻¹ in the second half of March. In the afternoon hours, enhancements of MTs/benzene ratio coincided with the highest temperature. While enhancements during the early morning hours (00-05 h) coincided with lowest temperature of the day. In contrast to isoprene, emissions of monoterpene are independent of light but exponentially dependent on ambient temperature (Mielke, 2010). Therefore, in the absence of sunlight, 275 higher MTs/isoprene ratios indicate significant nighttime biogenic emissions of monoterpenes. The lower ratios of MTs/isoprene persisted throughout the day suggest that the high radiation favored the isoprene emissions relative to monoterpenes (Ebben et al., 2012). During the midnight-early morning period, the average MTs/isoprene ratio of 0.25 ppbv ppbv⁻¹ in the first half of February increased to 0.43 ppbv ppbv⁻¹ in the second half of March (Fig 5c). The estimated change in MTs/isoprene ratio is 280 consistent as the change of ambient temperature in the early morning hours with significantly higher values in second half of March than those in the first half of February. The nighttime emission of monoterpenes would have caused the increase in ambient mixing ratio due to the development of the nocturnal boundary layer (NBL). Therefore, the nighttime enhancements of MTs/benzene ratio indicate the emissions from non-specific storage pool (Demarcke et al., 2010). It has been reported that the plants 285 accumulate pools of monoterpenes and store them in structures like resin ducts and glandular trichomes or related structures (Kuhn et al., 2002). The emission of isoprene generally depends upon both light and

temperature, whilst release of monoterpenes from plant storages may be exclusively by temperature and independent of light (Jones et al., 2011). In the afternoon and early morning hours, the ratios of MTs/isoprene were in the ranges of 0.1-0.2 ppbv ppbv⁻¹ and of 0.25-0.43 ppbv ppbv⁻¹, respectively. In the tropical rainforest of South-East Asian (SE Asian), the emission ratios of MTs/isoprene were measured in the range of 0.24-0.27 (Misztal et al., 2011). The daytime MTs/isoprene ratios measured in the present study are in good agreement with the average ratios of 0.23±0.3 derived from flux measurements at the Bukit Atur GAW station in SE Asian tropical rainforest (Langford et al., 2010). In fact, the MTs/isoprene ratio increased from ~0.3 during the day to ~2.0 during the night at Bukit Atur station (Jones et al., 2011). Guenther et al. (2008) report the MTs/isoprene emission ratios of ~0.15 for different tropical forests. The increasing trend of MTs/benzene ratio in the afternoon hours is consistent with the increase in ambient temperature during winter to summer transition. The average diurnal maximum of solar flux (temperature) increased from 667 W m⁻² (30 °C) in the first half of February to 767 W m⁻² (38 °C) in the second half of March.

In Fig. 5e-h, diurnal plots of monoterpenes mixing ratio, MTs/benzene ratio, ambient temperature and solar flux for clear-sky and cloudy days are compared to evaluate the sensitivity of biogenic emissions. On a cloudy day (15 February), mixing ratio of monoterpenes exhibited large variation and higher values compared to a clear-sky day (17 March). While MTs/benzene ratio showed opposite patterns to that of diurnal pattern of monoterpenes mixing ratio. In the afternoon hours, ratios of MTs/benzene on a clear-sky day were significantly higher than those observed on a cloudy day. The ratios of MTs/benzene for cloudy and clear-sky days were 0.21±0.08 ppbv ppbv⁻¹ and 0.60±0.22 ppbv ppbv⁻¹, respectively. Except some spikes, ratios of MTs/benzene followed the diurnal pattern of ambient temperature on both cloudy and clear-sky days.

4. Effect of local meteorology

4.1 Dependence on wind parameters

Meteorological parameters play a vital role in dispersion and accumulation of pollutants including short-lived VOCs in urban regions. Meteorological conditions can also influence biogenic emission processes through mechanical stress to plants and hence the mixing ratio of monoterpenes (Haase et al., 2011).

315 The relationships of monoterpenes mixing ratio with wind speed in February and March are shown in Fig. 6. Box-whisker plots using 10-minute interval data show the levels of different percentiles (5, 25, 75 and 95), mean and median in each wind speed bin (0.5 m s^{-1}). **In the lower wind speed regimes ($<3 \text{ m s}^{-1}$), the mixing ratio of monoterpenes and its variability (percentiles) declined with increasing winds. But showed small wind speed dependence in the higher wind speed regimes ($>3 \text{ m s}^{-1}$).** In February
320 (March), average mixing ratios were $0.75 \pm 0.84 \text{ ppbv}$ ($0.52 \pm 0.84 \text{ ppbv}$) and $0.20 \pm 0.84 \text{ ppbv}$ ($0.15 \pm 0.09 \text{ ppbv}$) under calm and windy conditions, respectively. The dependence of monoterpenes mixing ratio with wind speed can be represented by exponential decay functions.

$$\text{In February: } [\text{MTs}] = 0.661 \times \exp(-0.985 \times \text{WS}) + 0.166 \quad (1)$$

$$\text{In March: } [\text{MTs}] = 0.493 \times \exp(-0.496 \times \text{WS}) + 0.088 \quad (2)$$

325 In above equations, [MTs] is mixing ratio (ppbv) of monoterpenes and WS stands for wind speed (m s^{-1}). Comparison of fit parameters in Eq. (1) and (2) indicates that the decline rate of monoterpenes with increasing wind speed in February was much faster than that in March.

The ratio of MTs/benzene increased gradually from $0.20 \pm 0.25 \text{ ppbv ppbv}^{-1}$ under calm winds to $0.35 \pm 0.30 \text{ ppbv ppbv}^{-1}$ at higher winds ($5\text{-}6 \text{ m s}^{-1}$) in February. In March, the ratio showed a different
330 relationship with wind speed as it increased rapidly from 0.25 to $0.90 \text{ ppbv ppbv}^{-1}$ at lower wind speeds but showed sharp decline to $0.15 \pm 0.09 \text{ ppbv ppbv}^{-1}$ at higher wind speeds. The distinct relations between MTs/benzene ratio and wind speed in February and March suggest the significant roles of other factors. For example, unlike February, the higher wind speeds in March coincided with lower ambient temperatures (mostly below $30 \text{ }^\circ\text{C}$). Consequently, declines of MTs/benzene ratio at higher wind speeds
335 in March could be due to reduced biogenic emissions. Similarly, highlighting the impact of wind speed

Hasse et al. (2011) have reported a factor of 93% increase of monoterpenes mixing ratio during storms at the Thompson Farm site in Durham, New Hampshire.

To assess the wind direction dependence, we have used a polar frequency analysis of monoterpenes mixing ratio and MTs/benzene ratio (Fig. 7). The occurrence frequencies of different levels of monoterpenes and MTs/benzene are averaged in a bin of 22.5°. Winds were predominantly from the N-NE during both the months but presence of W-NW winds was also significant in March. In February (March), elevated mixing ratios of monoterpenes (>0.5 ppbv) and MTs/benzene ratios (>0.5 ppbv ppbv⁻¹) account for about 25% (18%) and 4% (14%) of total data, respectively. In other words, from winter-to-summer transition, mixing ratio of monoterpenes and ratio of MTs/benzene showed decreasing and increasing trends, respectively. In particular, the highest frequency of elevated monoterpenes was observed during northerly winds in February while during westerly winds in March. Overall, the elevated mixing ratios of monoterpenes were mostly observed during easterly (0-180°) winds in February, while during westerly (180-360°) winds in March. Mixing ratios of monoterpenes were about 0.35 ppbv during both easterly and westerly winds. However interestingly, the ratios of MTs/benzene differed significantly with average values of 0.21 ppbv ppbv⁻¹ in the easterly and 0.49 ppbv ppbv⁻¹ in the westerly winds. **The wind fields show the prevailing light winds during both the months of February and March (Fig. S4). The synoptic wind fields over the study regions suggest the flow from the north in February but mostly from the NW and westerly in March. As the magnitudes of the wind speed were very small, the transport of monoterpenes from distant sources could have very little influences. Therefore, also due to short atmospheric lifetime, the levels of monoterpenes measured at the study site are mainly due to the emissions in local and surrounding areas.** The wind direction dependence of MTs/benzene ratio clearly indicates higher contributions from biogenic sources located in the western regions. **The combined effect of NW and westerly winds and higher ambient temperatures in March provides favorable conditions for the local emissions and transport of BVOCs from the nearby areas.**

Photo-oxidation of monoterpenes leads to the formation of SOA and hence can cause significant reductions in atmospheric visibility. Atmospheric visibility in urban areas has been observed to show

positive correlations with wind speed and ambient temperature (Chen and Xie, 2013). We have analyzed the variation of monoterpenes mixing ratio and MTs/benzene ratio with visibility (Fig. 8). Mixing ratios of monoterpenes were high in the lower visibility conditions (<4 km) but showed lower values under high visibility conditions (>4 km). In February (March), the mixing ratio of monoterpenes decreased from 0.58 ± 0.4 (0.47 ± 0.22) ppbv at 1.5 km of visibility to 0.20 ± 0.2 (0.15 ± 1.2) ppbv at 5.5 km. While the ratio of MTs/benzene tends to increase with increasing visibility. In February (March), the MTs/benzene ratio increased from 0.011 ± 0.01 (0.19 ± 0.07) ppbv at 1.5 km of visibility to 0.24 ± 0.3 (0.30 ± 2.4) ppbv at 5.5 km.

4.2 Dependence on ambient temperature and sunlight

Ambient temperature is one of the most important parameters controlling emission of BVOCs. Variations of monoterpenes mixing ratio and MTs/benzene ratio with ambient temperature are shown in Fig. 9. The box plots represent the variability of 10-min data in different temperature bins for both daytime and nighttime. In February, MTs/benzene ratio exhibits little dependence while mixing ratio of monoterpenes tends to decrease with increasing temperature. The nighttime ratios of MTs/benzene measured at lower temperatures (< 21°C) do not show significant differences between February and March as the values were 0.23-0.27 ppbv ppbv⁻¹. But for higher nighttime temperatures (22-26°C), however recorded only in March, the MTs/benzene ratio increased from 0.29 ppbv ppbv⁻¹ at 22°C to 0.60 ppbv ppbv⁻¹ at 26°C. Unlike those in February, the daytime mixing ratio of monoterpenes shows sharp rise at higher temperatures (>30 °C) in March. In this month, the daytime mixing ratios of monoterpenes were 0.17 ± 0.02 ppbv at lower temperatures (<30 °C) and 0.35 ± 0.2 ppbv at higher temperatures (>30 °C). Overall including day and night, the MTs/benzene ratio in March gradually increased from 0.27 ± 0.2 ppbv ppbv⁻¹ at lower temperatures to 0.50 ± 1.5 ppbv ppbv⁻¹ at higher temperatures. In March, however at the respective higher temperatures, the nighttime enhancements of MTs/benzene were higher than those measured during the daytime. This could be due to photochemical

loss of monoterpenes leading to decrease of MTs/benzene ratios during the day. Nonetheless, the corrections due to photochemical aging will lead to even higher daytime ratios and more clearly establish the dependence on ambient temperature. Sunlight intensity is another significant factor controlling emission of BVOCs from vegetation. Variations of monoterpenes mixing ratio and MTs/benzene ratio with sunlight intensity are also shown in Fig. 9. In February, the ratio decreased slightly with increasing solar flux while mixing ratio of monoterpenes does not show a clear trend. In March, both monoterpenes mixing ratio and MTs/benzene ratio increased rapidly at lower intensities ($<150 \text{ W m}^{-2}$) but show no clear dependence at higher intensities. Quantitatively, the dependence of monoterpenes and MTs/benzene on ambient temperature is complicated due to several other competing and simultaneous processes. For example, emissions are high at higher temperatures, at the same time removal rates due to photo-oxidation and PBL dynamics are also high. Despite this complexity, significant increase in biogenic emissions of monoterpenes is due to change from winter to summer conditions. In monoterpene emitting vegetations, monoterpenes are stored in storage structures referred as pool including leaf cavities, glandular cells, resin canals and ducts. As a result, monoterpene emissions are mainly dependent on ambient temperature (Guenther et al., 2012).

4.3 Estimation of biogenic emissions and impact of other sources

Time series of monoterpenes mixing ratio and MTs/benzene ratio for the day and night periods are shown separately in Fig. 10. The nighttime mixing ratios exhibit strong variations in the range of 0.10-1.0 ppbv compared to daytime values of 0.08-0.48 ppbv. The daytime mixing ratios were consistently lower than the nighttime values from February until the first half of March but were comparable during the second half of March. In case of MTs/benzene ratio, the daytime ($0.16 \text{ ppbv ppbv}^{-1}$) and nighttime ($0.18 \text{ ppbv ppbv}^{-1}$) values are comparable in the first half of February. However, in the second half of March, the daytime ratio of $0.68 \text{ ppbv ppbv}^{-1}$ was significantly higher than the nighttime ratio of $0.31 \text{ ppbv ppbv}^{-1}$. Overall, the daytime mixing ratio of monoterpenes and ratio of MTs/benzene follow the trend of ambient temperature. The enhancements in the daytime monoterpenes mixing ratio and

MTs/benzene ratio coincide with the periods of higher temperatures when daily maximum exceeded 30 °C. Which were particularly noticeable when winds were predominantly from the W-N sector (270-360°). Overall, the daytime and nighttime mixing ratios of monoterpenes showed increasing and decreasing trends, respectively. In particular, very high nighttime mixing ratios were measured during periods of shallower PBL depths. **But MTs/benzene ratios during both day and night show increasing trends.**

A source-tracer-ratio (STR) method has been applied to estimate the contributions of local and regional sources to the abundance of anthropogenic and biogenic VOCs (Goldstein and Schade, 2000; Legreid et al., 2007; Borbon et al., 2013). The ambient mixing ratio of monoterpenes (MT) can be represented as the sum of contributions of primary anthropogenic (MT_A), biogenic (MT_B) and transport (MT_R) sources.

$$MT = MT_A + MT_B + MT_R \quad (3)$$

In Eq. (3), MT_A represents local contribution mainly from biomass/bio-fuel burning. During present study period, MT_R could represent contributions from both biomass burning and biogenic emission that have taken place at far distances. However, due to relatively short atmospheric lifetime of monoterpenes, values of MT_R are expected to be small or at least assumed to be constant during the study period (Sahu et al., 2017). Anthropogenic contribution can be estimated by using benzene as a marker (Wagner and Kuttler, 2014).

$$MT_A = (\Delta MT / \Delta \text{benzene}) \times \text{Mixing ratio of benzene} \quad (4)$$

Where, $\Delta MT / \Delta \text{benzene}$ is emission ratio (ER) estimated from the evening measurements influenced mainly by local anthropogenic sources and have not been significantly altered due to oxidation processes. Nonetheless, activities of biomass/bio-fuel burning in the city and nearby areas were negligible. Therefore, relative contribution of biogenic sources to monoterpenes mixing ratio can be estimated as here.

$$MT_B = MT - (\Delta MT / \Delta \text{benzene}) \times \text{Mixing ratio of benzene} \quad (5)$$

The average contributions from local biogenic sources to ambient monoterpenes were estimated to about 31%, 49%, 41% and 67% during 1-15 February, 16-28 February, 1-15 March and 16-31 March, respectively. Temporal trend of biogenic contribution follows the variation of daily maximum temperature to large extents. At the same time, it is important to take account of the fact that the biogenic contributions were lowest and highest during the winds from the N-E and W-N sectors, respectively. Therefore, the combined effect of ambient temperature and wind direction explains the overall trend of biogenic contribution. As shown in Figure 10, the mixing ratio of acetonitrile does not show any clear trend during the study period. The average daytime mixing ratios of acetonitrile were ~0.50 ppbv during the first half of February and second half of March (Table 1). Similarly, the nighttime values were almost same ~0.82 ppbv during the first half of February and second half of March. Therefore, the estimated trend of biogenic contribution is expected to have little influence of biomass/bio-fuel burning. The increase of about 36% from winter to summer conditions can be attributed to the change in biogenic emissions. This is more than 2 times higher than estimated that of isoprene (16%) during the same study period (Sahu et al., 2017). The biogenic emission trends are underestimated in view of expected increase of OH concentrations and hence increase in daytime removal of monoterpenes during winter-summer transition. The age corrected MTs/benzene ratio, particularly for the daytime data, will provide a better quantification of biogenic emissions but trend or relative change in biogenic contributions remain same assuming small change in OH. The major contributions to ambient monoterpenes are mostly due the emissions from local sources and impact of long-range transport is rather small due to short lifetime. This is consistent with the facts that variations of monoterpenes in ambient air showed strong dependence on several local meteorological parameters. The emissions in local or nearby areas can be due to both anthropogenic and biogenic sources. According to the relative estimates presented in this study, anthropogenic emissions contribute ~69% during the first half of February. On the other hand, the anthropogenic contributions to measured monoterpenes in reduced to ~33% in the second half of March. This change is mainly attributed to the increase of biogenic emissions as the meteorological conditions were more favorable during the second half of March. However, the changes in relative contributions of two different emission sources are

465 mainly to the change in biogenic contributions. As it is clarified, except for some events, the emissions from biomass burning did not show any clearly trend during study period.

5. Conclusions

Variation of monoterpenes and impact of meteorological parameters were examined in the context of the transition from winter-to-summer at an urban site of India. Mixing ratios of monoterpenes (m/z 137.131 and m/z 81.07) were measured using PTR-TOF-MS 8000 instrument during February-March 2014. The data presented in this study is one of the best available measurements in India owing to high time- and mass- resolutions of PTR-TOF-MS. The meteorological parameters showed significant changes with prevailing winds shifted from northerly in February to westerly in March. Large increases in monoterpenes are observed under warm and calm conditions. Mixing ratio of monoterpenes showed strong diurnal dependence with elevated values from evening till midnight hours and lowest in the afternoon. Some sporadic local biomass burning events including the bonfire during *Holi* festival caused exceptionally high levels of monoterpenes in ambient air. Daily mixing ratio of monoterpenes does not show clear trend with monthly means of about 0.35 ppbv for both the months. The impact of biogenic emissions could not be discerned in mixing ratio data due to competing influence of PBL dynamics and OH-reaction loss processes. However, the MTs/benzene ratios of 0.68 ppbv ppbv⁻¹ in the daytime and 0.31 ppbv ppbv⁻¹ in the nighttime during second half of March were 2-3 times higher their respective values during the first half of February. Mixing ratio of monoterpenes declined with increasing wind speed which is well represented by the exponential decay functions. However, rate of decline in February was about 2 times greater than that in March. MTs/benzene ratio shows strong response with ambient temperature as it increased from 0.27 ppbv ppbv⁻¹ (<30°C) to 0.50 ppbv ppbv⁻¹ (>30°C). The increase of about 36% in biogenic contributions of monoterpenes during winter-to-summer conditions can be attributed mainly to local sources. The higher nighttime ratios of monoterpenes/isoprene indicate significant light-independent but temperature dependent emissions of monoterpenes. Overall, the combined effect of westerly winds and higher temperatures in March provided favorable conditions for

the local emissions and regional transport of monoterpenes. This study clearly highlights the strong sensitivity of **monoterpenes** emission to the meteorological conditions at semi-arid urban site. At the same time, the inherent complexities due to post-emission processes limit the scope of this data for emission estimates. Therefore, flux measurements of **monoterpenes and other** BVOCs are highly recommended which will provide emission characteristics in different ecosystems of tropical India. This study highlights the importance of BVOCs considering the policies of improving air quality in tropical urban regions. The need of regional representations of BVOCs, particularly of monoterpenes, has been emphasized in the state-of-art models of atmospheric aerosols (Browne et al., 2014).

Except of isoprene, the chemical scheme of other BVOCs for SOA formation is not coupled in the global models such as the Goddard Earth Observing System Chemistry Climate Model (GEOS CCM). As a representative for the western region of the Indian subcontinent, this study will be important for the parameterizations of monoterpene emission in the models which do not necessarily take into account of change in formation and release rates under extreme and episodic changes in weather conditions. The measurements of BVOCs emitted from terrestrial vegetations in the tropical regions of South and Southeast Asia (S-SE Asia) are very important where data are very sparse. However, their role in atmospheric chemistry is complex due to the vast geography with different climatic zones and co-existence of a variety of natural and anthropogenic sources. There is a need to establish a network of stations for the measurements of BVOCs over the Indian subcontinent. The priority should be to obtain the representative measurements for the emission from tropical rainforest (Western Ghats), temperate forest (lower Himalayas) and vegetations in central (tropical deciduous forest) of India.

Data availability. The data used in this study are available in figshare repository (<https://figshare.com/s/15ff9a338f800b163c83>).

515 *Author contribution.* In this study, Dr. Lokesh Sahu has designed the experiment. The data analysis was done and also original manuscript was written by Nidhi Tripathi. The corrections and revision in manuscript were made by Dr. Sahu.

Competing interests. The coauthor of this article agrees that he has no objection in publishing this work.

520 *Acknowledgements.* The weather data are taken from the Automatic Weather Stations (AWS) of the Indian Space Research Organisation (ISRO) and wunderground.com. The measurement data presented in this study are available with Dr. Lokesh Kumar Sahu (lokesh@prl.res.in).

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Table 1: The average \pm standard deviation values of monoterpenes, acetonitrile, MTs/benzene ratio and meteorological parameters measured at Ahmedabad during the first half of February and second half of March, 2014.

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Species	01-15 Feb 2014		16-31 Mar 2014	
	<i>Day</i>	<i>Night</i>	<i>Day</i>	<i>Night</i>
Monoterpenes (ppbv)	0.19 \pm 0.12	0.41 \pm 0.28	0.40 \pm 0.25	0.46 \pm 0.30
MTs/benzene (ppbv ppbv ⁻¹)	0.18 \pm 0.04	0.16 \pm 0.04	0.68 \pm 0.50	0.31 \pm 0.14
Acetonitrile (ppbv)	0.51 \pm 0.15	0.83 \pm 0.37	0.47 \pm 0.18	0.82 \pm 0.39
Benzene (ppbv)	0.94 \pm 0.45	2.6 \pm 1.4	0.90 \pm 0.60	2.1 \pm 1.6
Temperature (°C)	30 \pm 4	19 \pm 2	36 \pm 2	27 \pm 2
Wind speed (m s ⁻¹)	2.79 \pm 0.82	1.55 \pm 0.56	2.76 \pm 0.54	1.71 \pm 0.64
Pressure (hPa)	1011 \pm 2	1011 \pm 2	1010 \pm 2	1010 \pm 2
RH (%)	27 \pm 8	53 \pm 7	23 \pm 7	38 \pm 5

Figure captions

730 **Figure 1:** Top panel (A) shows the map of India and land use pattern of Ahmedabad city and surrounding areas (prepared using Bhuvan, the ISRO's Earth visualization portal (<https://bhuvan.nrsc.gov.in/>) and bottom panel (B) shows the number of major trees in Ahmedabad city and emission rates of monoterpenes for different plants taken from Singh et al., (2011) as ER 1 and Malik et al. (2018) as ER 2.

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Figure 2: Time series of hourly and daily (box-whisker) monoterpenes (MTs) mixing ratio, MTs/benzene ratio, meteorological parameters and planetary boundary layer (PBL) depth at Ahmedabad from 01 February to 31 March 2014.

740 **Figure 3:** The time series mixing ratios of MTs, acetonitrile and **benzene**, and **MTs-acetonitrile** correlation plots during two major episodes of biomass burning (a, b) for 19-20 February and (c, d) for 15-16 March, *Holi* festival.

Figure 4: Relations of monoterpenes mixing ratio and MTs/benzene ratio with acetonitrile during (a) February and (b) March 2004.

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Figure 5: Average diurnal profiles of monoterpenes (MTs) mixing ratio, MTs/benzene ratio, MTs/isoprene ratio, temperature and solar flux during (a-d) four different periods of 1-15 February, 16-28 February, 1-15 March and 16-31 March 2014 and (e-h) for a cloudy day (15 February) and clear-sky day (17 March).

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Figure 6: Variations of monoterpenes mixing ratio and MTs/benzene ratio with wind speed during the months of February (left panel) and March 2014 (right panel).

755 **Figure 7:** Polar frequency (%) plots of monoterpenes mixing ratio and MTs/benzene ratio during the months of February 2014 (left panel) and March 2014 (right panel).

Figure 8: Variation of monoterpenes mixing ratio and MTs/benzene ratio with atmospheric visibility in February (left panel) and March 2014 (right panel).

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Figure 9: Dependencies of monoterpenes mixing ratio and MTs/benzene ratio with ambient temperature separately for the daytime and nighttime of measurements and solar flux during February 2014 (left panel) and March 2014 (right panel).

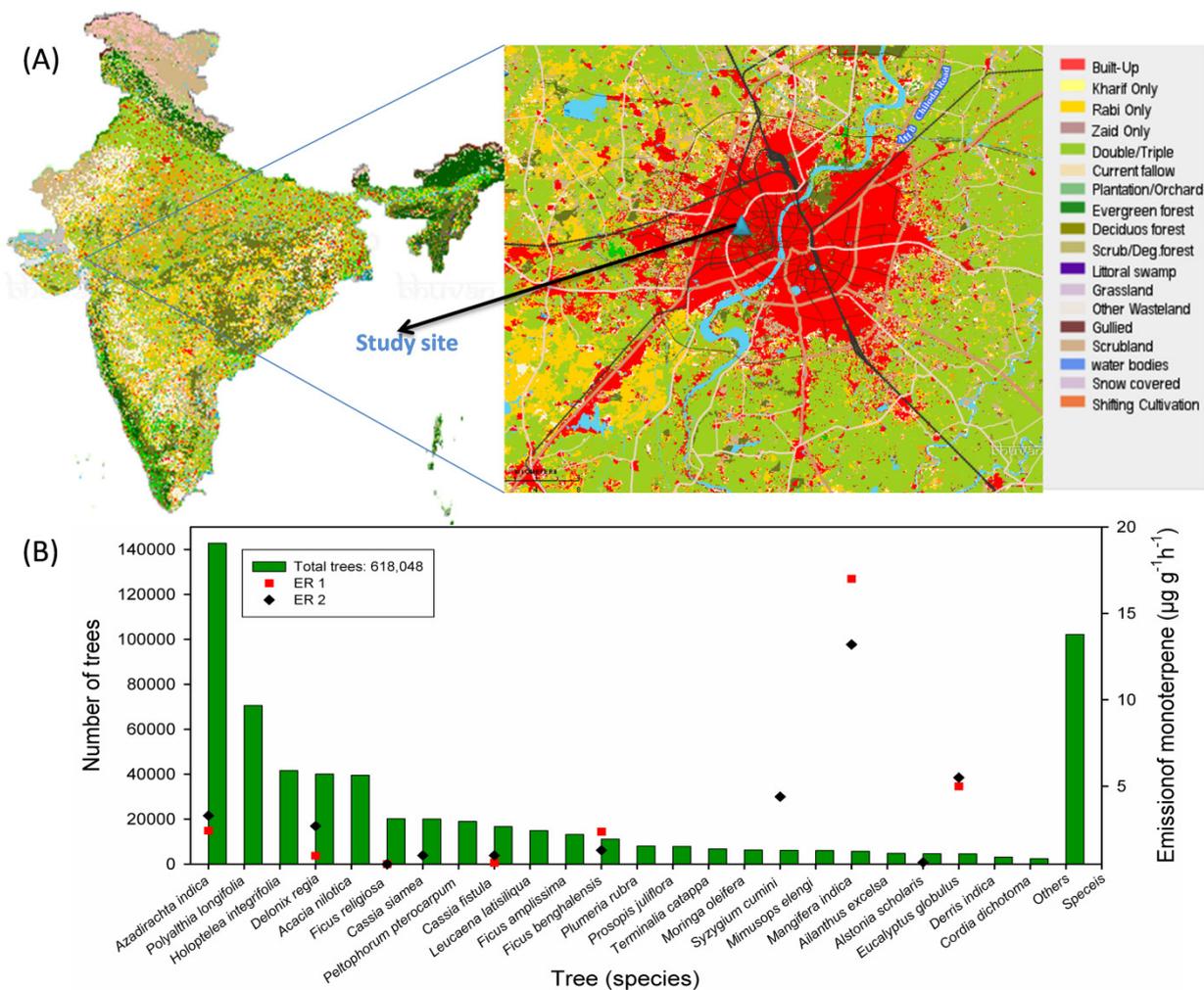
765 **Figure 10:** Time series of monoterpenes mixing ratio, MTs/benzene ratio, acetonitrile mixing ratio and estimated biogenic contribution along with daily air temperatures and percentage occurrence of winds from different sectors.

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790 **Figure 1:** Top panel (A) shows the map of India and land use pattern of Ahmedabad city and surrounding areas (prepared using Bhuvan, the ISRO's Earth visualization portal (<https://bhuvan.nrsc.gov.in/>) and bottom panel (B) shows the number of major trees in Ahmedabad city and emission rates of monoterpenes for different plants taken from Singh et al., (2011) as ER 1 and Malik et al. (2018) as ER 2.

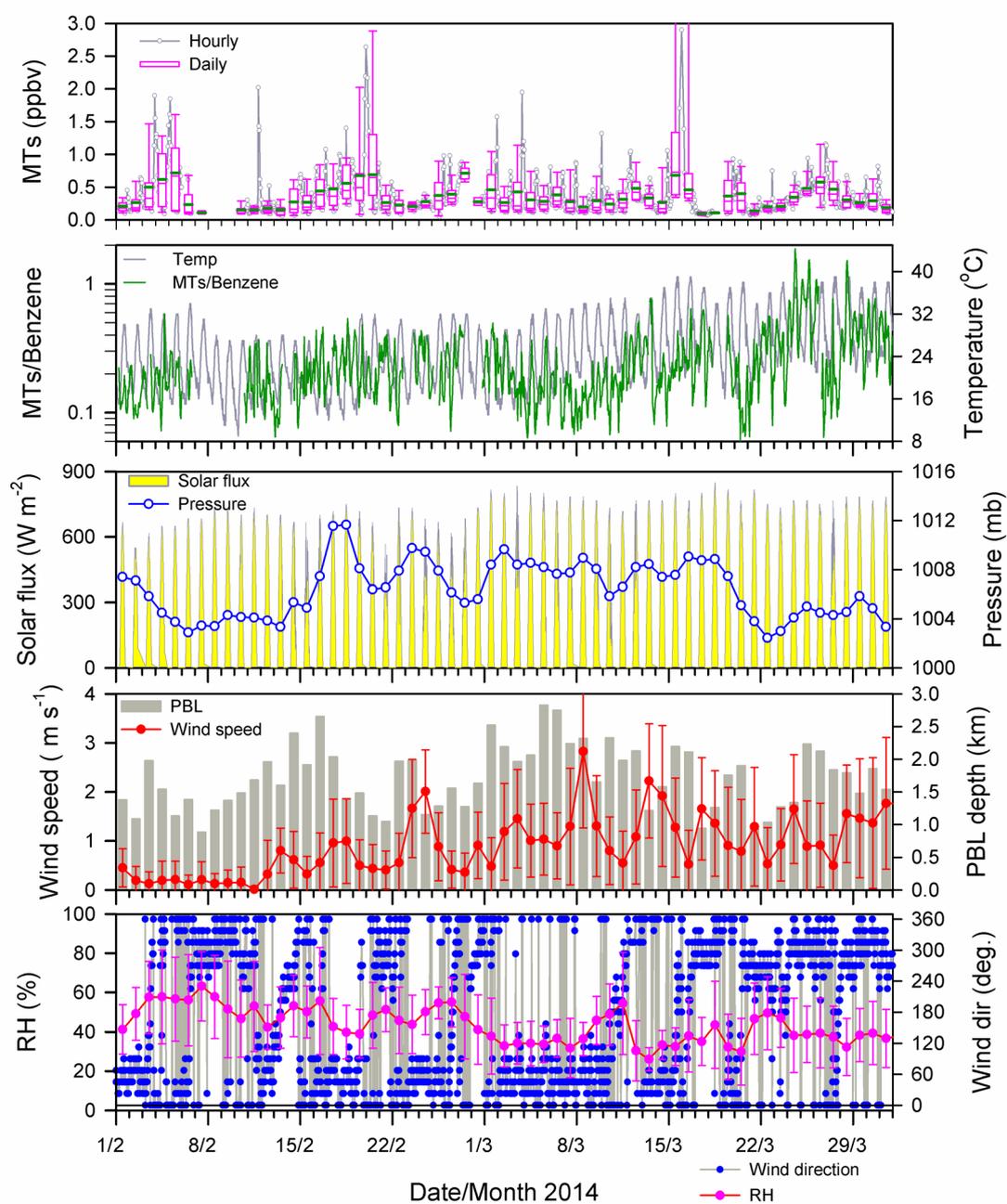
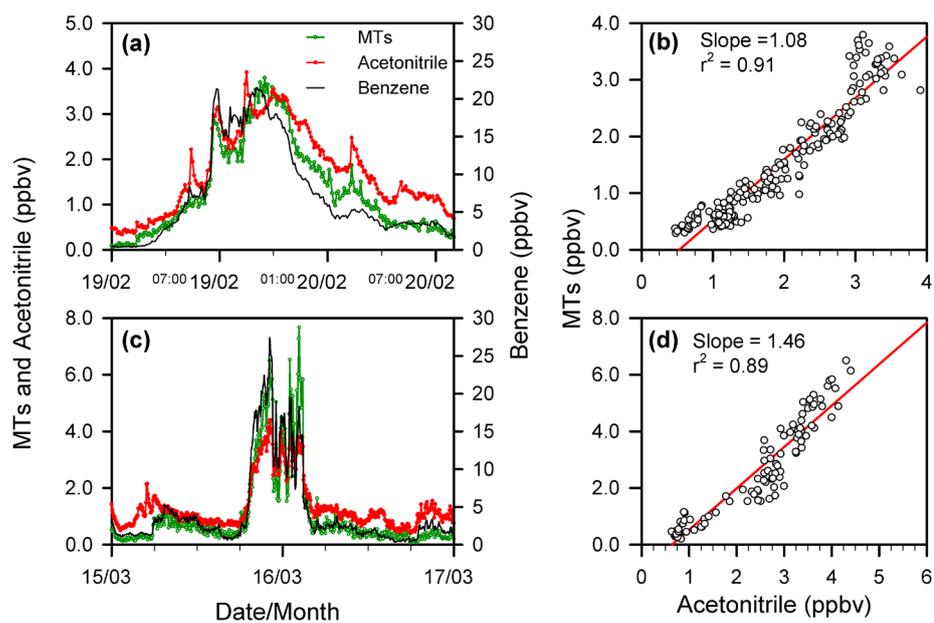


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805 **Figure 3:** The time series mixing ratios of MTs, acetonitrile and benzene, and MTs-acetonitrile
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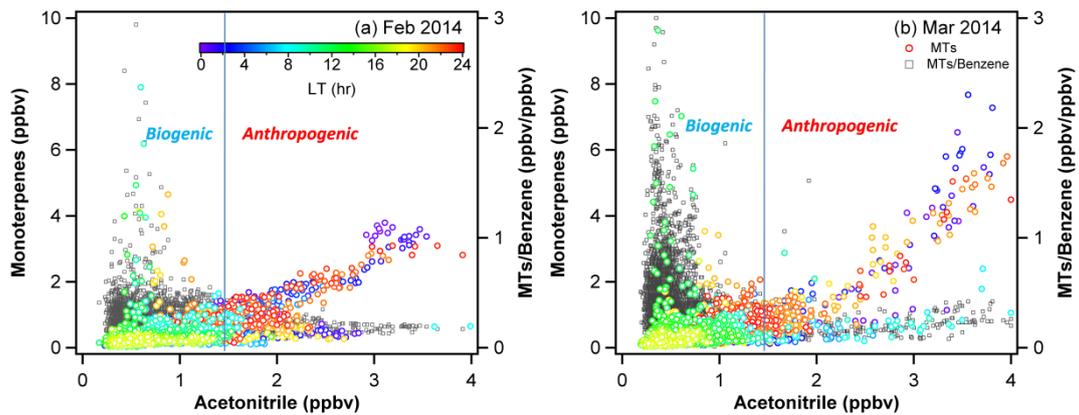


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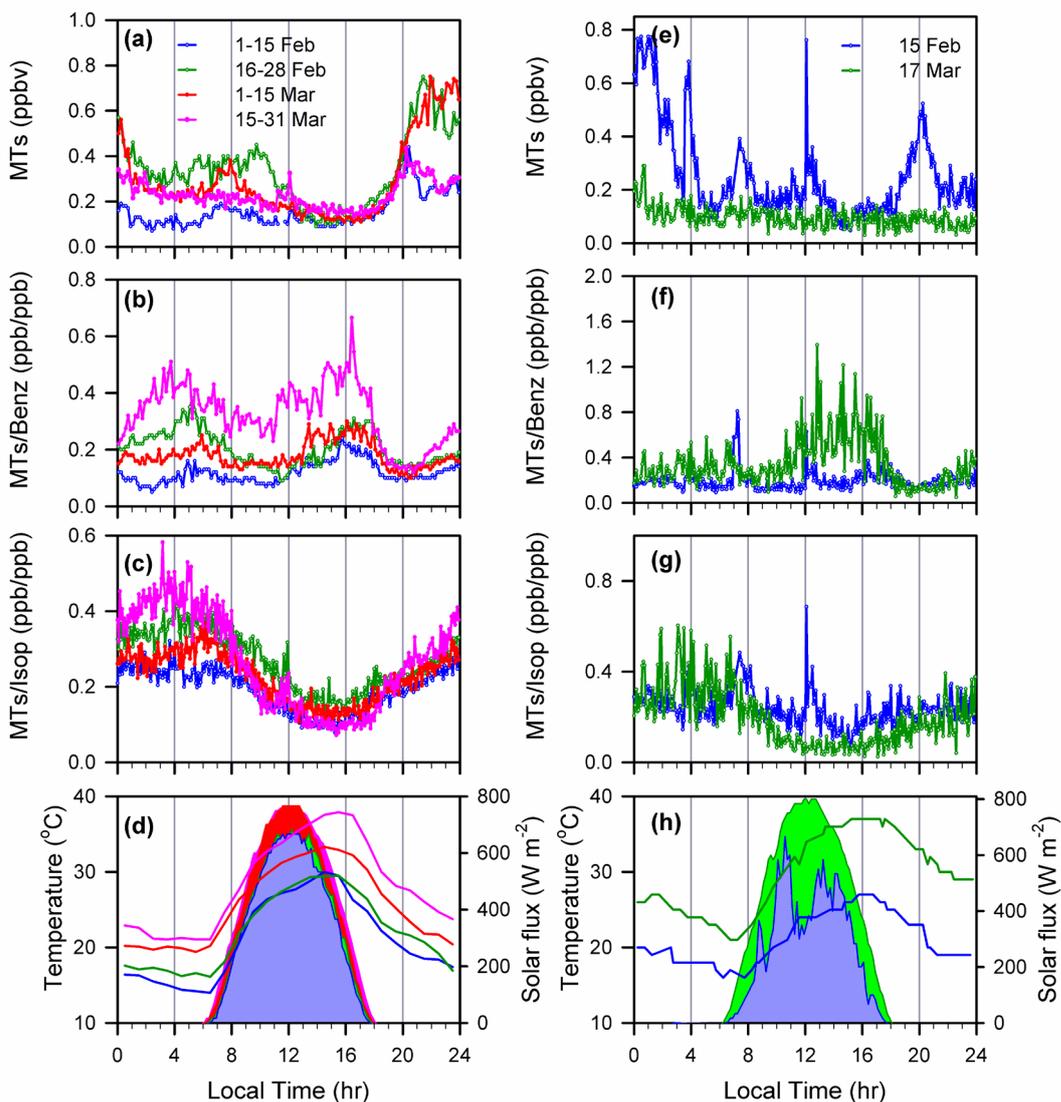


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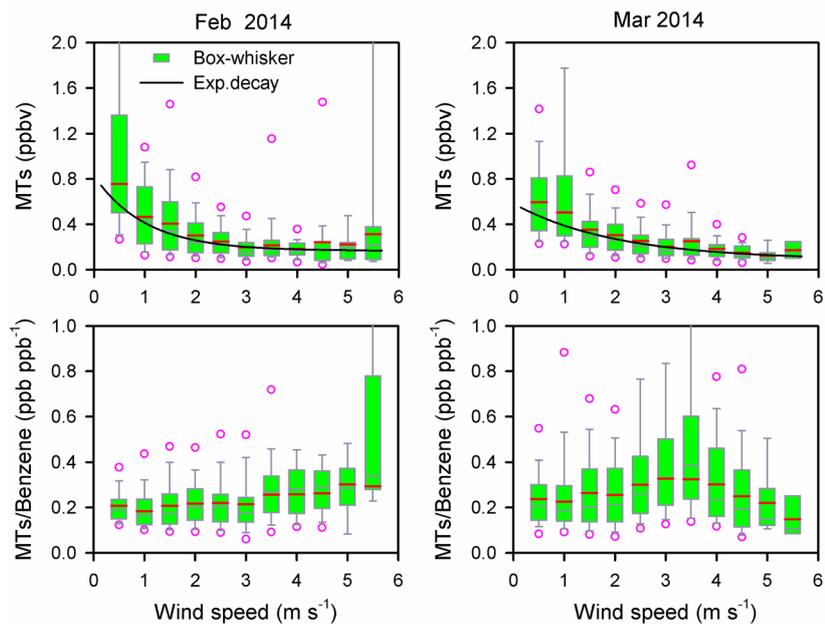


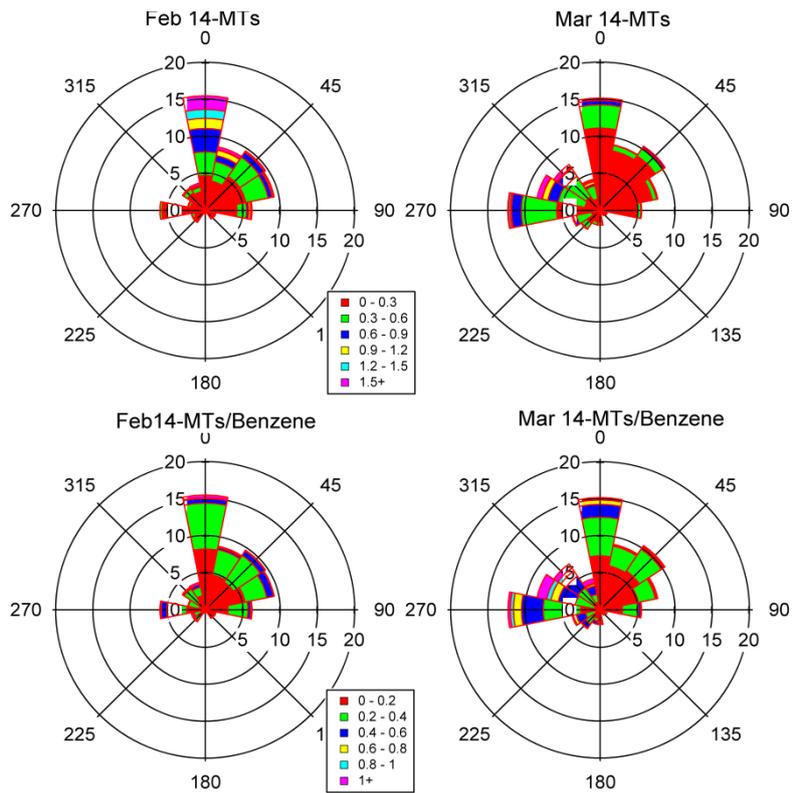
Figure 6: Variations of monoterpenes mixing ratio and MTs/benzene ratio with wind speed during the months of February (left panel) and March 2014 (right panel).

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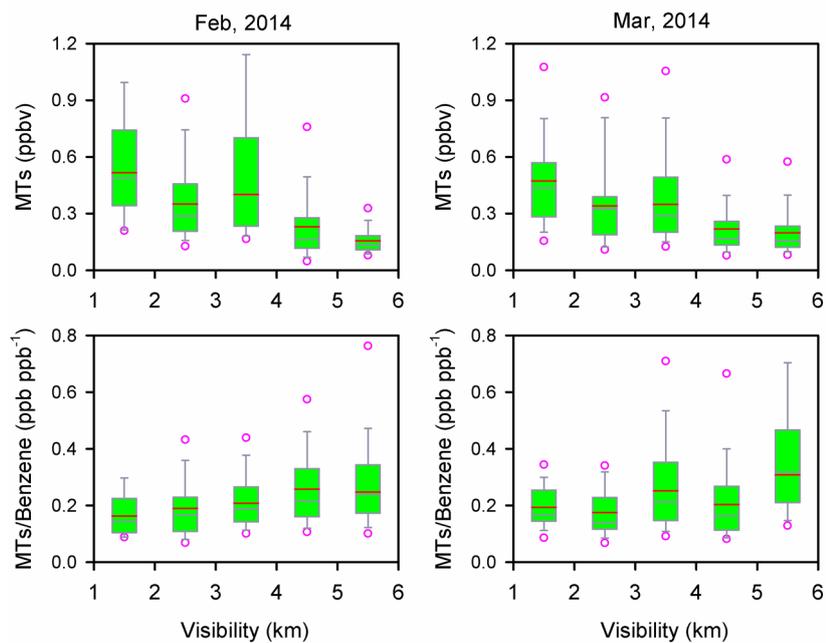


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Figure 7: Polar frequency (%) plots of monoterpenes mixing ratio and MTs/benzene ratio during the months of February 2014 (left panel) and March 2014 (right panel).

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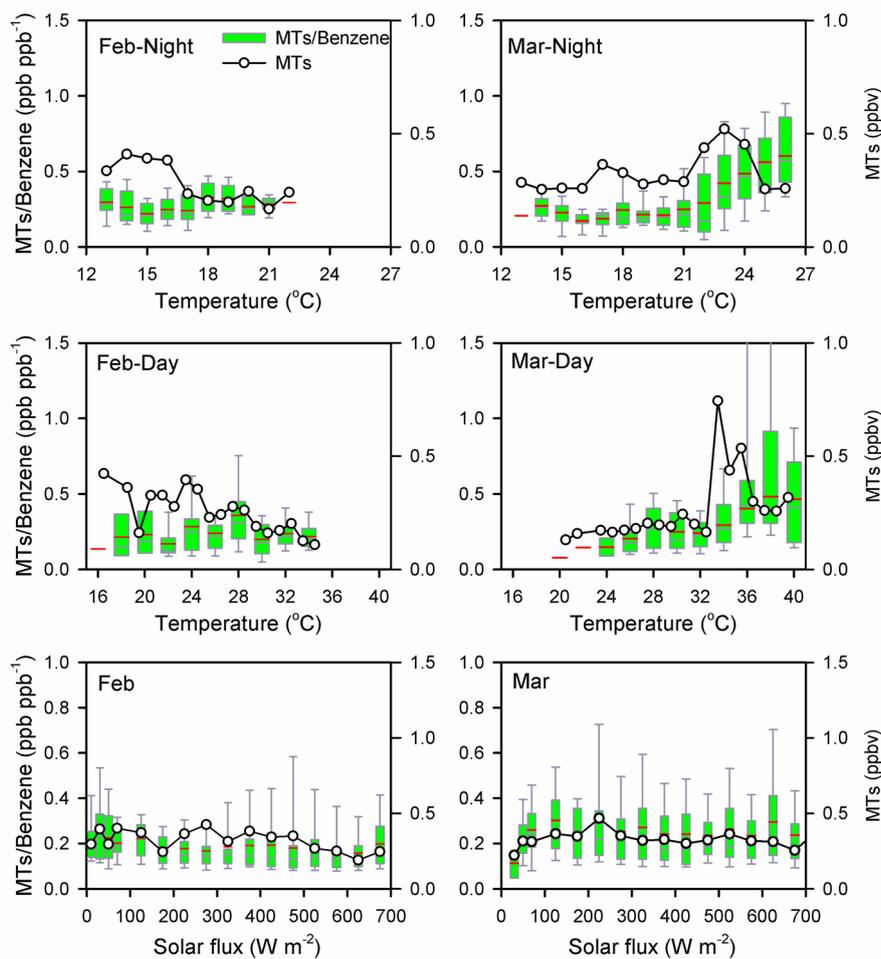


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900 **Figure 9:** Dependencies of monoterpenes mixing ratio and MTs/benzene ratio with ambient
 905 temperature separately for the daytime and nighttime of measurements and solar flux during
 910 February 2014 (left panel) and March 2014 (right panel).

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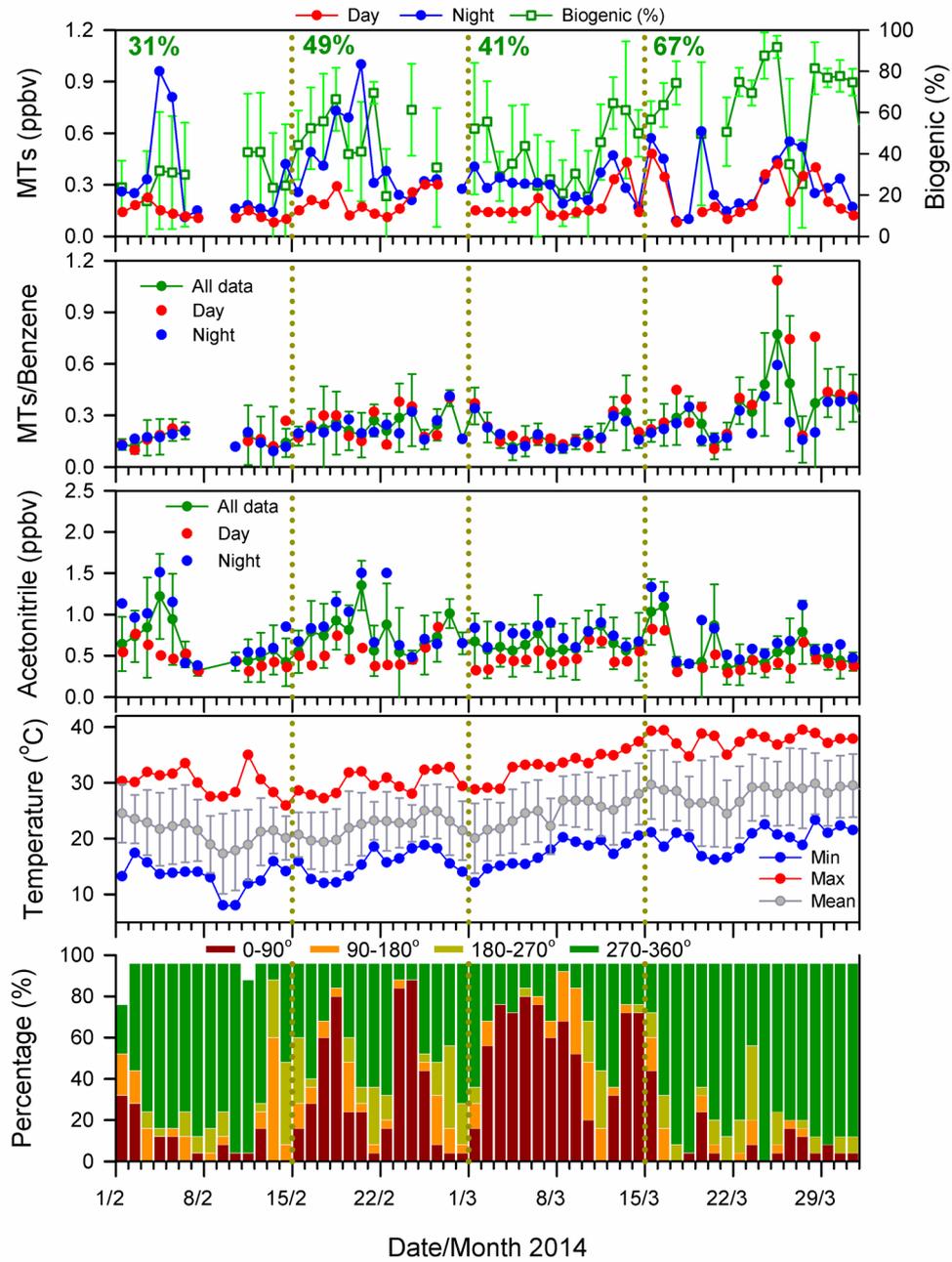


Figure 10: The daily median time series of monoterpenes mixing ratio, MTs/benzene ratio, acetonitrile mixing ratio and estimated biogenic contribution along with daily air temperatures and percentage occurrence of winds from different sectors.