

## **Response to Anonymous Referee # 2**

**We have done major revisions based on comments and suggestions to bring out important results with clarity. The revised manuscript also includes the revisions suggested by two other referees. Point-to-point answers (bold-font) to comments (Referee # 2) are given here.**

Referee Comment: General Comments: The manuscript entitled “Enhancement of biogenic emissions of VOCs in the semi-arid region of India during winter to summer transition period: Role of meteorological conditions” by Nidhi Tripathi and Lokesh Kumar Sahu reports high monoterpene mixing ratios using PTR-TOF-MS in Ahmedabad, India. The authors suggest that the monoterpenes mixing ratios show increasing trend from evening to midnight due to high temperature. They have also tried to establish the biogenic contribution to monoterpenes using monoterpenes/benzene emission ratios and from regional transport. Although the manuscript provides information about biogenic and anthropogenic sources of monoterpenes from a part of the world where VOC data are scarce, it lacks scientific significance and needs to be presented in a more convincing way to the readers. The manuscript is not logically written and not well organized. It was very hard to understand what the main points are in the result and discussion section. Therefore, I recommend that the manuscript needs major revision and cannot be accepted for publication in ACP in the current format.

**Author’s Reply: Thank you for providing valuable general comments and we have revised the manuscript based on all comments. We have done further analysis of data to make improve the discussion and conclusion. The manuscript has been reorganized to make it more logical. We agree that the focus of this paper is mainly on MTs but not necessarily isoprene or other BVOCs, accordingly suggested changes are made. The objective has been clearly defined as here.**

**Please see following in Revised MS, Lines 80-82:**

**“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.**

Specific Comments: Title: The title “Enhancement of biogenic emissions of VOCs: : :” doesn’t reflect the content of the manuscript in my opinion. In this manuscript, the authors tried to investigate the emission sources (that includes both biogenic and anthropogenic sources such as biomass burning and during Holi festival) of monoterpenes in the semi-arid region in India. As isoprene is the primary biogenic VOC and authors did not discuss the biogenic emission sources of isoprene in detail, I think the title does not justify the content of the manuscript and it needs to be revised.

**Author’s Reply: We agree that the focus of this paper is mainly on MTs but not necessarily on other BVOCs such as isoprene. In addition to biogenic emissions, role of anthropogenic**

sources (mainly biomass burning) are also discussed with more details. Therefore, as also suggested by the referee, we have revised the title as here: **“Emissions and atmospheric concentrations of monoterpenes in a semi-arid region of India: Role of winter to summer changes in meteorological conditions”**

Referee Comment: Abstract:

P1, L10-11: The authors themselves mentioned here that “This study is based on the measurements of monoterpenes” which was exactly what I pointed out in the Title of the manuscript.

**Author’s Reply: Based on this and earlier comments we have revised the Title of the paper. “Emissions and atmospheric concentrations of monoterpenes in a semi-arid region of India: Role of winter to summer changes in meteorological conditions”**

P1, L12: The authors should mention the months here when they mention “winter-to summer transition”

**Author’s Reply: We have revised and mentioned the months as here.**

**Please see following in Revised MS, Lines 10-13:**

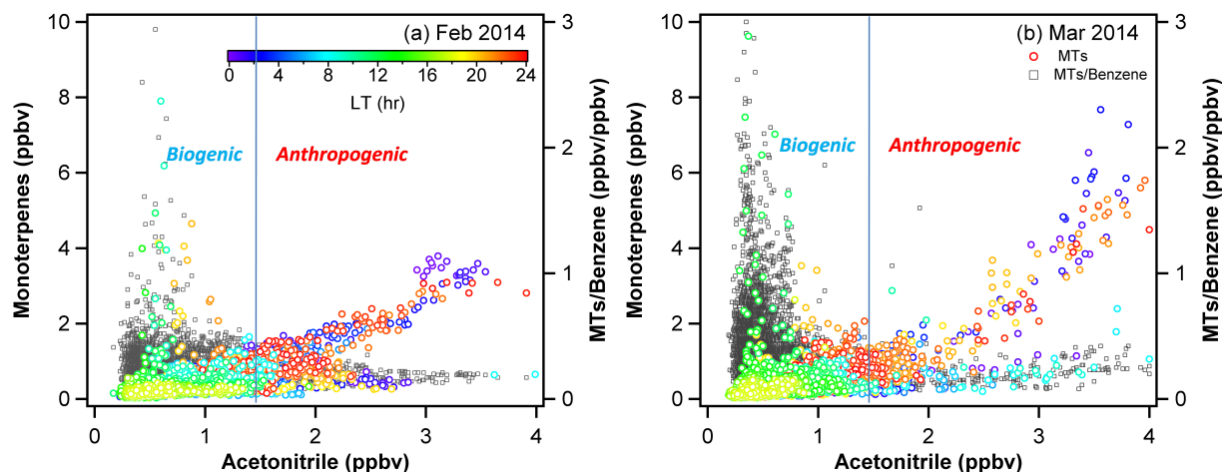
**“This study is based on the measurement of monoterpenes using a proton transfer reaction-time of flight-mass spectrometer (PTR-TOF-MS) at a semi-arid site in western India during winter-to-summer transition period of February-March 2014.”**

P1, L13-16: These sentences are kind of confusing to the readers. The authors first mentioned that “monoterpenes showed strong diurnal variation with elevated values from evening till midnight and lowest in the afternoon.” Nighttime elevated monoterpenes mixing ratios cannot be attributed to biogenic emissions entirely as there can be contributions from other anthropogenic sources. This nighttime emission sources of monoterpenes need to be investigated in detail. The next sentence they mentioned “The daily data does not show clear trends with monthly means of ~0.35 ppbv during each month”. This contradicts with the previous sentence where it is mentioned that “monoterpenes showed strong diurnal variation: : :” In addition, if we look at Table 1, the monthly means for February and March is different. Therefore, “monthly means of ~0.35 ppbv during each month” doesn’t make any sense.

**Author’s Reply: Thank you for this nice analysis and we have understood that as there were lacks of clarification leading to confusion or sense of contradictions. As discussed in the paper that analysis of mixing ratio data alone is not sufficient to discuss about the contribution from different sources due to variations in met and PBL parameter. As already mentioned, signatures of biogenic emissions in the mixing ratio data are obscured due to dominating influence of PBL. Hence there is a clear distinction between ‘diurnal’ and ‘daily’ in case it is leading to confusion. 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. Therefore, the MTs/benzene ratio has been used to refer the biogenic emissions. Agreeing to the comments, we have further investigated the**

nighttime emissions and following additional explanations have been provided in the revised version.

Please see following in Revised MS, Lines 220-229 and Fig 4:



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 ( $< 1$  ppbv). For lower acetonitrile concentrations, the ratios increased from  $\sim 0.24$  ppbv ppbv $^{-1}$  in February to  $0.40$  ppbv ppbv $^{-1}$  in March. But for higher acetonitrile values ( $> 1$  ppbv), the lower ratios of  $\sim 0.18$  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.

The major nighttime enhancements of MTs mixing ratio during 16-19 February were associated with the dips in daily minima to  $12-13^{\circ}\text{C}$ . On the other hand, no such enhancements can be noticed in MTs/benzene ratio. Therefore, the change in emissions at least from anthropogenic sources seems to play rather minor role. The significant episodic changes in nighttime mixing ratios of MTs during the second half of February were mainly controlled by the variations in meteorological parameters. In the second half of the March, the increase in MTs/benzene ratio during the night and day hours were due to increase of daily minimum and maximum temperatures, respectively. Therefore, in this study, the MTs/benzene ratio is a better parameter to understand the trends of biogenic contribution but not really the MTs mixing ratio only. Supporting the increasing biogenic contribution during winter-summer transition, the MTs/benzene ratios measured during both day and night hours increased significantly from the first half of February to second half of March (Table 1).

We have revised also Figure 8 (now Figure 9) and also provided more details on nighttime emission sources such as here. (Please see following in Revised MS, Lines 375-381).

**“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<sup>-1</sup>. But for higher nighttime temperatures (22-26°C), however recorded only in March, the MTs/benzene ratio increased from 0.29 ppbv ppbv<sup>-1</sup> at 22°C to 0.60 ppbv ppbv<sup>-1</sup> at 26°C.”**

Referee Comment: Section 1: The authors should provide only the information relevant to the manuscript. If the authors are trying to focus only to address biogenic emissions, they should avoid providing information about anthropogenic emissions such as in P2,L40: “Major sources of anthropogenic VOCs (AVOCs) include combustion of fossil fuel, biomass burning, use of solvents, industrial production, refineries, etc.(Sahu, 2012).”and elsewhere. The authors should also rearrange the information they want to provide in the Introduction section. Currently, it reads like several information gathered from previous works and the authors put that in the introduction section but most of the places there is no connection between the previous sentence and the next one which confuses the readers and is hard to follow. Additionally, the authors should cite some previous work performed in urban areas in South Asia using PTR-TOF-MS e.g. Sarkar et al. (2016) reported a valuable dataset from urban Kathmandu Valley using PTR-TOF-MS. Sarkar, C., Sinha, V., Kumar, V., Rupakheti, M., Panday, A., Mahata, K. S., Rupakheti, D., Kathayat, B., and Lawrence, M. G.: Overview of VOC emissions and chemistry from PTR-TOF-MS measurements during the SusKat-ABC campaign: high acetaldehyde, isoprene and isocyanic acid in wintertime air of the Kathmandu Valley, *Atmos. Chem. Phys.*, 16, 3979-4003, <https://doi.org/10.5194/acp-16-3979-2016>, 2016.

**Author’s Reply: We agree that the information presented in the “Introduction” section look scattered with several facts though important but may be irrelevant. Now, we have revised the Introduction section by considering the suggestions and removed irrelevant parts. We have also referred the previous works including Sarkar et al., 2016. The revisions are highlighted (red color font), we request the referee to please go through the “Introduction” section of the revised version.**

Referee Comment:

Section 2: Authors should provide detailed information regarding the PTR-TOFMS calibrations i.e. how many calibrations were performed during the measurement period, details of the standard and dilution flows of GCU, sensitivity plots, how the sensitivities varied during the measurement period and effect of RH on MT sensitivity. How was the transmission curve of the PTR-TOF looks like? How was the estimation of monoterpenes mixing ratios using at m/z 137.131 performed since monoterpenes fragmentation also gives signal at 81.070? How often was the zero-air test performed in a day and during the measurement period? All this detailed information should be there (within the manuscript or as a supplementary information) to establish that the data presented in the manuscript is reliable.

**Author's Reply:** We have taken all care to ensure the high quality and reliability of data. As suggested by the referee, we have also provided detailed Supplementary Information and discussions related to PTR-TOF-MS calibrations including the effect of RH on MT sensitivity and transmission curve. A schematic set-up of calibration system is also provided in the supplementary information. The monoterpenes mixing ratio estimated using  $m/z$  137.131 by taking account the sensitivity of product at 81.07 is also elaborated in the supplementary information. In addition, we have also revised the relevant parts of section 2 (2.Measurement site and PTR-TOF-MS instrumentation).

Please see following in Revised MS, Lines 126-148:

“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 ( $\text{C}_{10}\text{H}_{16}\text{-H}^+$ ) and by taking account of its product at  $m/z$  81.07 ( $\text{C}_6\text{H}_8\text{-H}^+$ ). A certified gas mixture containing  $0.97 \text{ ppmv} \pm 5\%$  of  $\alpha$ -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 ( $\alpha$ -pinene) among other VOCs. Therefore, in the calibration, the detected fragmentation at  $m/z$  81.07 was only due to  $\alpha$ -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( $\text{C}_6\text{H}_6$ ), isoprene ( $\text{C}_5\text{H}_8$ ), acetonitrile ( $\text{CH}_3\text{CN}$ ) 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).”

Referee Comment:

Section 3.1: Is the measurement site  $\alpha$ -pinene dominant? Monoterpenes fragmentation pattern depends on instrumental condition as well as different monoterpene species as shown in Tani et al., 2004. Thus, if this site is characterized as an  $\alpha$  -pinene dominant area, the uncertainty in estimating MT concentration can be minimized. Otherwise,  $m/z$  137.131 reported in this study will imply a big uncertainty. Therefore, if this is the former case, please provide appropriate references or data.

**Author's Reply:** As shown in Figure 1, tree species like *Mangifera indica*, *Eucalyptus globules*, *Ficus benghalensis*, *Syzygium*, etc. are major  $\alpha$ -pinene emitters for which emissions of isoprene were reported (e.g., Varshney and Singh, 2003; Padhy and Varshney, 2005 and references therein). So the biogenic emissions of  $\alpha$ -pinene and isoprene co-exist, we have revised for the same as here:

Please see following in Revised MS, Lines 104-108:

**“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  $\alpha$ -pinene emitters for which emissions of isoprene were reported (e.g., Padhy and Varshney, 2005; Varshney and Singh, 2003 and references therein).”**

Referee Comment:

Section 3.2: P8, L198: 16 March P8, L202-205: What about the MT/acetonitrile ratios during nighttime for rest of the measurement period? The authors are emphasizing here on the emission of MT from biomass burning during the evening till next early morning during the Holi festival. However, in many places of the manuscript, the authors ignored this fact of biomass burning contribution to MT mixing ratios and emphasizing only on emissions from storage pool from plants due to high temperature during nighttime. The activity of biomass and wood burning is a common practice in India at evening and nighttime during wintertime.

**Author's Reply:** We agree with your points and have revised the manuscript with following additional analysis.

The relations (or dependencies) of both MTs and MTs/benzene ratio on CH<sub>3</sub>CN using all data points measured during the months of February and March are presented separately in Figure 4. This analysis clears the confusion and highlights the parts of data tagged as biogenic and anthropogenic. We have also revised Figure 9 (Now Figure 10) and provided time series of CH<sub>3</sub>CN separately for both the daytime and nighttime measurements. Accordingly the discussion has been revised. In summary, we have not denied the role of biomass burning but the contributions of biogenic emissions have been focused to see the changes associated with winter-to-summer transition in key met parameters.

Following revision can be noticed.

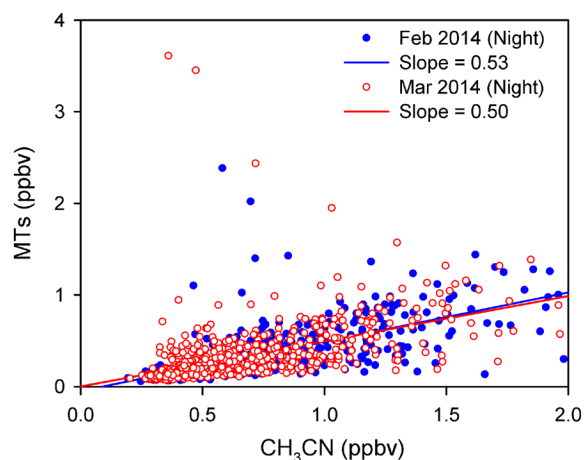
Please see following in Revised MS, Lines 95-98

**“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.”**

And Revised MS, Lines 212-215

**“For the rest of the measurement period, the nighttime  $\Delta$ MTs/ $\Delta$ CH<sub>3</sub>CN slopes of  $\sim 0.5$  ppbv ppbv<sup>-1</sup> were determined separately for February and March months. These lower nighttime  $\Delta$ MTs/ $\Delta$ CH<sub>3</sub>CN slopes clearly highlights that the most of the data were not directly influenced by the biomass burning plumes.**

”



(Scatter plots between the nighttime mixing ratios of MTs and CH<sub>3</sub>CN are shown separately for February and March 2014. The data measured during two biomass burning plumes are excluded)

Referee Comment: Section 3.3: P10, L246-250: The statement “Therefore, in the absence of sunlight, higher MTs/isoprene ratios indicate higher nighttime biogenic emissions of monoterpenes than those of isoprene.” is absurd as biogenic emission of isoprene do not occur at night. The authors should explain how they estimated isoprene mixing ratios as in urban areas isoprene could be overestimated due to isomers from other sources. For instance, in smoke the “isoprene peak” is 20% pentadiene + cyclopentene. What about the contribution of 232-MBO to isoprene mixing ratios? It is well known that isoprene emissions can occur from traffic and BB and that can rationalize nighttime isoprene and contribute to daytime isoprene. Isoprene can have ~20% interferences though from other compounds even at high mass resolution (Yokelson et al. 2013, Sarkar et al, 2016) in fresh smoke. Can the author estimate the fraction of observed isoprene from vegetation and combustion? P11, L263: MT/isoprene ratios during early morning clearly indicates that there is anthropogenic contribution to the MT mixing ratios.

**Author’s Reply:** This is an important point and we have revised as suggested. About P10, L246-250: Thank you for this we fully agree but we did not to mean convey this. Now we have rectified this mistake and rephrased the sentence as here.

Please see following in Revised MS, Lines 274-275

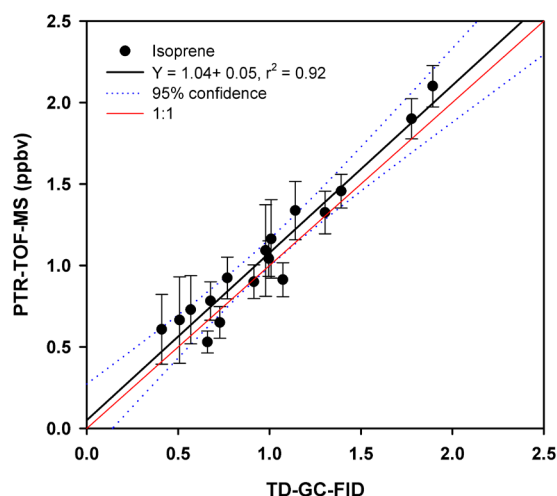
“Therefore, in the absence of sunlight, higher MTs/isoprene ratios indicate significant nighttime biogenic emissions of monoterpenes.

About interferences: First, the contribution of furan in isoprene (m/z 69.0699) is clearly separated from isoprene owing to the high mass resolutions ( $m/z > 5000$ ) of PTR-TOF-MS. However, several compounds or their fragments such as cyclopentene, pentanal, 2-methyl-3-buten-2-ol (MBO), etc. may interfere with the mass of isoprene. The concentrations of such interfering compounds are particularly significant near the

petrochemical industries and biomass burning sources (Warneke et al., 2010; Yokelson et al. 2013). The study site is far away from the petrochemical and biomass burning (fresh smoke) sources hence the interferences of such compounds are considered as minor (Sahu et al., 2016). For sure there is anthropogenic contribution to monoterpenes. In this paper, there is a dedicated section about the role of anthropogenic sources (3.2 Impact of biomass burning) including Figure 3. Except for a few events (e.g., *Holi* festival), strong biomass burning plumes were not detected as referred from CH<sub>3</sub>CN data.

**About garbage fires and leaf litter burning:** The policies of local governments are very strict and biomass burning such as garbage fires and leaf litter burning are prohibited. The scenario is very different than those in the Indo-Gangetic Plain (IGP) and several other parts of the country where activities of biomass burning are rampant in winter. In ambient air, fragments of biogenic MBO contributing to isoprene and may also alter the response.

Chromatographically, isoprene and MBO elute at different temperatures and provide individual mixing ratios for MBO and isoprene (Kaser et al., 2013). However, for limited periods, we also operated both TD-GC-FID and PT-TOF-MS systems simultaneously and compare the measurements of aromatics and isoprene. Based on comparison of ambient isoprene measurements, the  $(\text{PTR-TOF-MS})_{\text{isoprene}}/(\text{TD-GC-FID})_{\text{isoprene}}$  ratio of  $\sim 1.04$  (ppb/ppb) were determined using the bi-variate analysis which indicates a good agreement between the two instruments for April 2017. Details of our TD-GC-FID system are presented in our previous papers (Sahu et al., 2016b and Yadav et al., 2019).



In case, isoprene data may be subject to some additional uncertainties but its use has been limited to qualitative inferences (MTs/isoprene) and does not induce uncertainties in the estimates of biogenic emissions. We have revised the manuscript for above points (see supporting information).

## References:

Kaser, L., Karl, T., Schnitzhofer, R., Graus, M., Herdinger-Blatt, I. S., DiGangi, J. P., Sive, B., Turnipseed, A., Hornbrook, R. S., Zheng, W., Flocke, F. M., Guenther, A.,



**Keutsch, F. N., Apel, E., and Hansel, A.: Comparison of different real time VOC measurement techniques in a ponderosa pine forest, *Atmos. Chem. Phys.*, 13, 2893-2906, <https://doi.org/10.5194/acp-13-2893-2013>, 2013.**

**Sahu, L. K., Pal, D., Yadav, R. and Munkhtur, J.: Aromatic VOCs at major road junctions of a metropolis in India: measurements using TD-GC-FID and PTR-TOF-MS instruments, *Aerosol Air Qual. Res.*, 16, 2405–2420, doi:10.4209/aaqr.2015.11.0643, 2016.**

**Warneke, C., de Gouw, J. A., Del Negro, L., Brioude, J., McKeen, S., Stark, H., Kuster, W. C., Goldan, P. D., Trainer, M., Fehsenfeld, F. C., Wiedinmyer, C., Guenther, A. B., Hansel, A., Wisthaler, A., Atlas, E., Holloway, J. S., Ryerson, T. B., Peischl, J., Huey, L. G., and Case Hanks, A. T.: Biogenic emission measurement and inventories determination of biogenic emissions in the eastern United States and Texas and comparison with biogenic emission inventories, *J. Geophys. Res.*, 115, D00F18, doi:10.1029/2009JD012445, 2010.**

**Ravi Yadav, L K Sahu, Nidhi Tripathi, D Pal, G Beig, SNA Jaaffrey, (2019), Investigation of emission characteristics of NMVOCs over urban site of western India, *Environmental Pollution*, 252, 245-255.**

**Yokelson, R. J., Burling, I. R., Gilman, J. B., Warneke, C., Stockwell, C. E., de Gouw, J., Akagi, S. K., Urbanski, S. P., Veres, P., Roberts, J. M., Kuster, W. C., Reardon, J., Griffith, D. W. T., Johnson, T. J., Hosseini, S., Miller, J. W., Cocker III, D. R., Jung, H., and Weise, D. R.: Coupling field and laboratory measurements to estimate the emission factors of identified and unidentified trace gases for prescribed fires, *Atmos. Chem. Phys.*, 13, 89-116, <https://doi.org/10.5194/acp-13-89-2013>, 2013.**

Referee Comment: Section 4.1: P12, L290-293: It was unclear to me what authors are trying to say here since both the sentences read contradictory to me. P13, L332-333: “Mixing ratios of monoterpenes were high in the lower visibility conditions (< 4 km) but showed lower values under high visibility conditions (> 4 km)” Shouldn’t it be the opposite since reduction of visibility will cause after the photooxidation of MT? Figure 4. a) and Figure 5: The diurnal profile and variations of nighttime MT mixing ratios seems highest from 16-28 February as compared to the other periods which contradicts the conclusions drawn by the authors that MT mixing ratios are higher during March than February.

**Author’s Reply: Thank you for this suggestion; we have revised the manuscript as here:**

**Related to P12, L290-293:**

**Please see following in Revised MS, Lines 317-319:**

**In the lower wind speed regimes (<3 m s<sup>-1</sup>), 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 m s<sup>-1</sup>).**

**Related to P13, L332-333:**

About the relations with the visibility, it is a preliminary result and nothing much has been concluded. If the referee/Editor suggests for the removal of this small part, we are ready to do this. Related to Figure 4. a) and Figure 5 [Now Figure 5. a) and Figure 6]:

We agree, this remark by referee is about MTs concentration is correct but pattern is other way round for MTs/ Benzene ratio. And this is an important point why we have relied on the variation or changes with respect to a tracer (benzene). Again, we clarify that transition in biogenic emissions were not gradual and were marked by episodes of lows and highs in ambient concentrations MTs which are consistent with the changes in key met parameters. Conclusion was not based on such daily or episodic variations, instead we have always maintained “in the first half of February” to “second half of March” while referring to the winter-summer transition. As explained in the paper that the MTs data alone (without reference to traces or met data) is insufficient to investigate the role of biogenic emissions and that is why we used MTs/Benzene ratio. In any case, wherever required, we have revised the manuscript to address this concern.

Please see following in Revised MS, Lines 240-246:

“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.”

*Once again we are thankful to the referee for insightful comments and suggestions.*