

Supplement of

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

Nidhi Tripathi^{1,2} and Lokesh Kumar Sahu^{1*}

¹Physical Research Laboratory (PRL), Navrangpura, Ahmedabad, 380009, India

²Indian Institute of Technology Gandhinagar Palaj, Gandhinagar, India

*Correspondence to: L. K. Sahu (lokesh@prl.res.in)

Supplement of section “2. Measurement site and PTR-TOF-MS instrumentation”

(A) Background (Zero) and Calibration

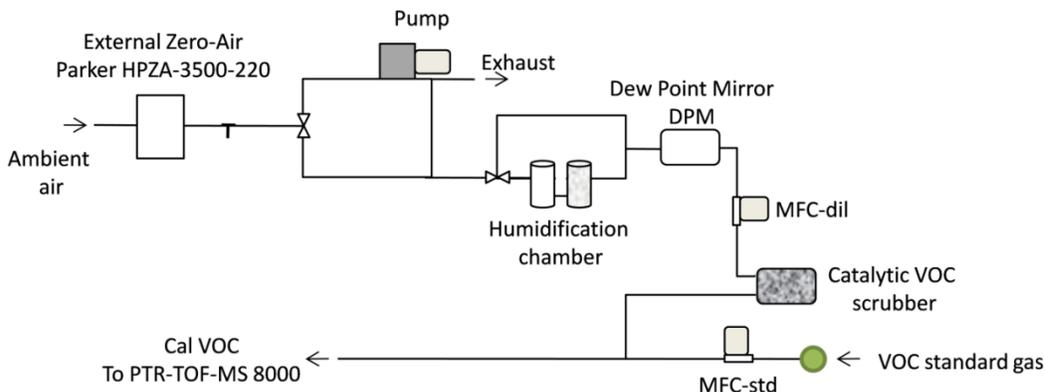


Figure S1. Schematic experimental set-up of gas calibration unit (GCU) used for the determination of instrumental background (zero) and multi-point calibration of PTR-TOF-MS 8000.

For the multi-point calibration of PTR-TOF-MS 8000, we used the dynamic dilution of a standard mixture using a gas calibration unit (GCU) (GCU-advanced v2.0, Ionicon Analytik GmbH, Innsbruck, Austria). The standard gas flow rate was adjusted using a mass flow controller (MFC-std) to provide variable quantities of standard gas into the dilution gas (zero air) flow of 500 sccm/min (typically) maintained using another MFC-dil. In GCU, the zero-air was generated by a heated (350°C) VOC-scrubber catalyst. We ensured the high stability of zero-air for determination of the background hence to quantify the overall performance of PTR-TOF-MS including sensitivity. Therefore, instead of using ambient air (with variable VOC) as input in GCU, we connected ultra purity (99.9999%) zero air generator (Parker HPZA-3500-220) in tandem with GCU. The desired relative humidity (RH) of zero-air air was generated by adjusting the set dew point temperature in the dew point mirror (DPM) unit. The instrumental background (zero) and calibration at different RH levels were performed about every 2- and 10-day of intervals, respectively. The background level (zero) is important for determination of the limit of detection (LOD). The LOD of MTs (25 pptv) was determined as $[2 \times (\text{standard deviation of background/sensitivity})]$ using 20-min time series data measured with 30s time resolution. As

reported in our previous study (Sahu et al., 2016), for a typical operating condition, high mass resolution ($m/\Delta m$) of about 5000 was achieved for the PTR-TOF-MS which enabled the identification of isobaric compounds (e.g., furan and isoprene) and fragments of different ions.

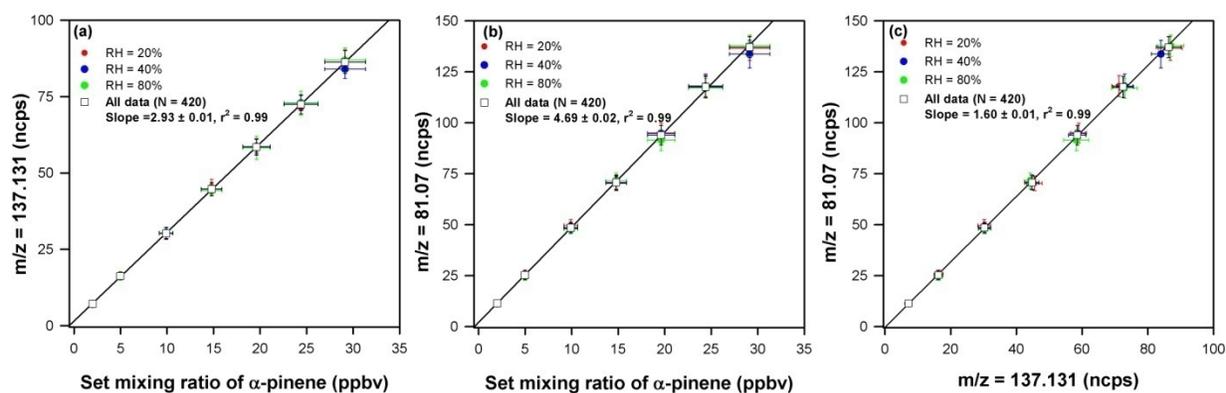


Figure S2. The scatter plots show the responses of (a) m/z at 13.131 and (b) m/z at 81.07 to different set mixing ratios of α -pinene, while (c) shows the relations between these two masses (m/z at 13.131 and m/z at 81.07).

The signals of both the ions (m/z at 13.131 and 81.07) and their relation show very small relative humidity (RH)-dependent response as investigated for RH values of about 20%, 40% and 80%. Statistical parameters reported in the legends were determined using the bivariate analysis considering the variations in both X and Y axes. Signals measured at m/z 137.131 and m/z at 81.07 represent about 40% and 60% of α -pinene. The product ion distributions of α -pinene are comparable with those reported in Kari et al., (2018) if minors ions ($\sim 4\%$) are ignored for the similar PTR-drift set-up of $E/N = 130$ Td in the PTR-TOF-MS 8000. The relative proportion of these two product signals are within the range of values reported in several studies (e.g., Misztal et al., 2011 and references therein). A sum of the product signals is used for quantification of total monoterpenes by taking account for the variation in the relative proportion at variable RH (Tani et al., 2003; Tani et al., 2004). Therefore, the total (summed) response due to these masses was taken account by multiplying the response determined at m/z 137.131 by a factor of 2.60, so that RH-dependence (although very small) is considered. Signals at m/z 137.131 and 81.07 were calibrated with 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 as they were not present in the standard (calibration) mixture. In this analysis a total of about 420 data points measured during different periods are considered.

(B) Transmission Efficiency:

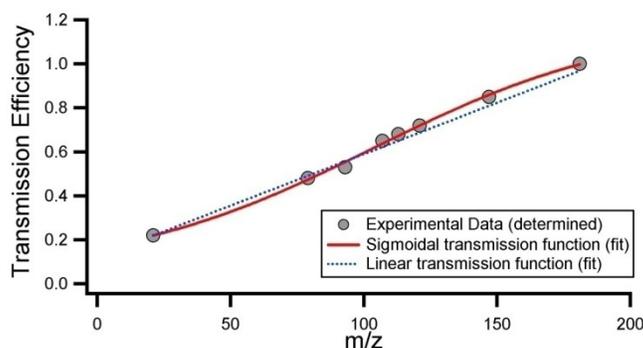


Figure S3. Relative transmission efficiency of PTR-TOF 8000 with sigmoidal and linear fits. However, it is to be noted that a gas standard (calibration) mixture was used to determine the sensitivity factors for different compounds (not by directly using the transmission fits).

(C) About Isoprene data:

About interferences: First, the contribution of furan in isoprene (m/z 69.0699) is clearly separated from isoprene owing to the high mass resolutions ($\Delta m/m > 5000$) 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. 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 ~ 1.04 (ppb/ppb) were determined using the bi-variate analysis which indicates a good agreement between the two instruments for the summer season (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.

Supplement of section “4.1 Dependence on wind parameters”

(A) Wind Fields

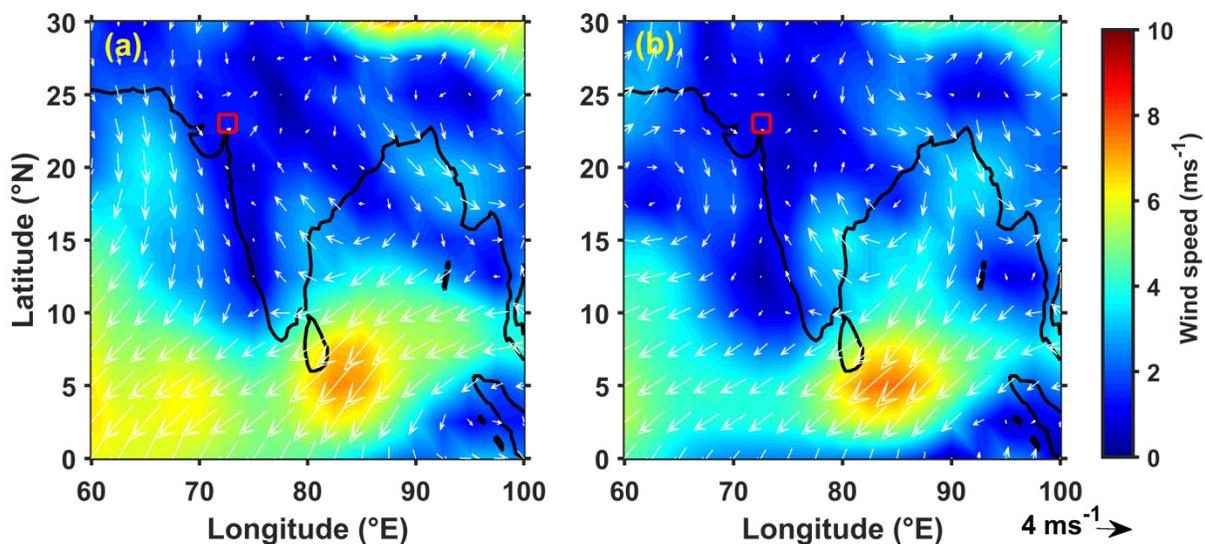


Figure S4: The mean wind fields at 925 mb pressure level over the Indian sub-continent during (a) February (b) March 2014. The red square symbol represents the study region. The wind field data were taken from the National Centers for Environmental Prediction (NCEP).

References:

- Kari, E., Miettinen, P., Yli-Pirilä, P., Virtanen, A., and Faiol, C. L. (2018). PTR-ToF-MS product ion distributions and humidity-dependence of biogenic volatile organic compounds. *Int. J. Mass Spectrom.* 430, 87–97. doi: 10.1016/j.ijms.2018.05.003.
- 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.
- Misztal, P. K., Nemitz, E., Langford, B., Di Marco, C. F., Phillips, G. J., Hewitt, C. N., MacKenzie, A. R., Owen, S. M., Fowler, D., Heal, M. R., and Cape, J. N.: Direct ecosystem fluxes of volatile organic compounds from oil palms in South-East Asia, *Atmos. Chem. Phys.*, 11, 8995–9017, doi:10.5194/acp-11-8995-2011, 2011.
- Sahu, L., Yadav, R. and Pal, D.: Source identification of VOCs at an urban site of western India: Effect of marathon events and anthropogenic emissions, *Journal of Geophysical Research: Atmospheres*, 121(5), 2416–2433, doi:10.1002/2015JD024454, 2016a.
- 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, 2016b.
- Tani, A., Hayward, S., and Hewitt, C. N.: Measurement of monoterpenes and related compounds by proton transfer reaction-mass spectrometry (PTR-MS), *Int. J. Mass Spectrom.*, 223, 561–578, 2003.
- Warneke, C., de Gouw, J. A., Del Negro, L., Brioude, J., McKee, 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.
- Tani, A., Hayward, S., Hansel, A., and Hewitt, C. N.: Effect of water vapour pressure on monoterpene measurements using proton transfer reaction-mass spectrometry (PTR-MS), *Int. J. Mass Spectrom.*, 239, 161–169, 2004.
- 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.