



Introduction

- IUPAC defines volatile organic compounds (VOCs) as organic compounds that have high vapour pressure ($> 10\text{ Pa}$ at 25°C) and low boiling point ($\leq 260^\circ\text{C}$).
- Volatile organic compounds (VOCs) are important as they play a major role in the oxidation chemistry of the atmosphere leading to the formation of ozone and secondary organic aerosols, which are important for air quality and climate. Moreover, certain VOCs have direct health impacts (e.g. benzene).
- In this study, ambient concentrations of VOCs such as methanol, acetone, acetonitrile, isoprene, acetaldehyde, toluene, benzene, sum of xylenes and sum of trimethyl benzenes were measured at ppt level sensitivity for the first time during the monsoon season over any Indian site from June - September 2013 in Mohali, a representative suburban site in the N.W. IGP [30.667°N ; 76.729°E ; N.W. IGP].
- The VOC measurements were performed every minute using a high sensitivity proton transfer reaction mass spectrometer at the IISER Mohali Atmospheric Chemistry Facility located in Mohali [30.667°N ; 76.729°E]. Time series of the one-minute data acquired during monsoon 2013 was analyzed and certain rain events and plume events were selected for detailed analysis of emission ratios and wet scavenging.
- Wet scavenging refers to the natural processes by which a material is removed by atmospheric hydrometeors (cloud and fog drops, rain, snow) and is consequently delivered to the Earth's surface. Wet scavenging is a very important cleansing mechanism of the atmosphere and yet it is poorly understood. We investigated the scavenging efficiency of monsoon rainfall for the aforementioned ambient reactive VOCs. The effects of various factors such as the boundary layer dilution effect, photochemistry and change in fetch region was systematically ascertained to derive the concentration differences purely attributable to wet scavenging.
- The processes of uptake and release of gases from the cloud or rain droplets is formulated following the Henry's law equilibrium in models. This remains to be experimentally validated for VOCs. This work is the first attempt worldwide to examine wet scavenging efficiency for the aforementioned VOCs using in-situ data.

Site description and meteorology



Figure 1: Map of the land use in a $100\text{ km} \times 200\text{ km}$ area surrounding the measurement site (black dot) in the city of Mohali in the North-West Indo-Gangetic plain (30.667°N , 76.729°E , 310 m a.s.l.) (Sinha et al., Atmos. Chem. Phys. 2014).

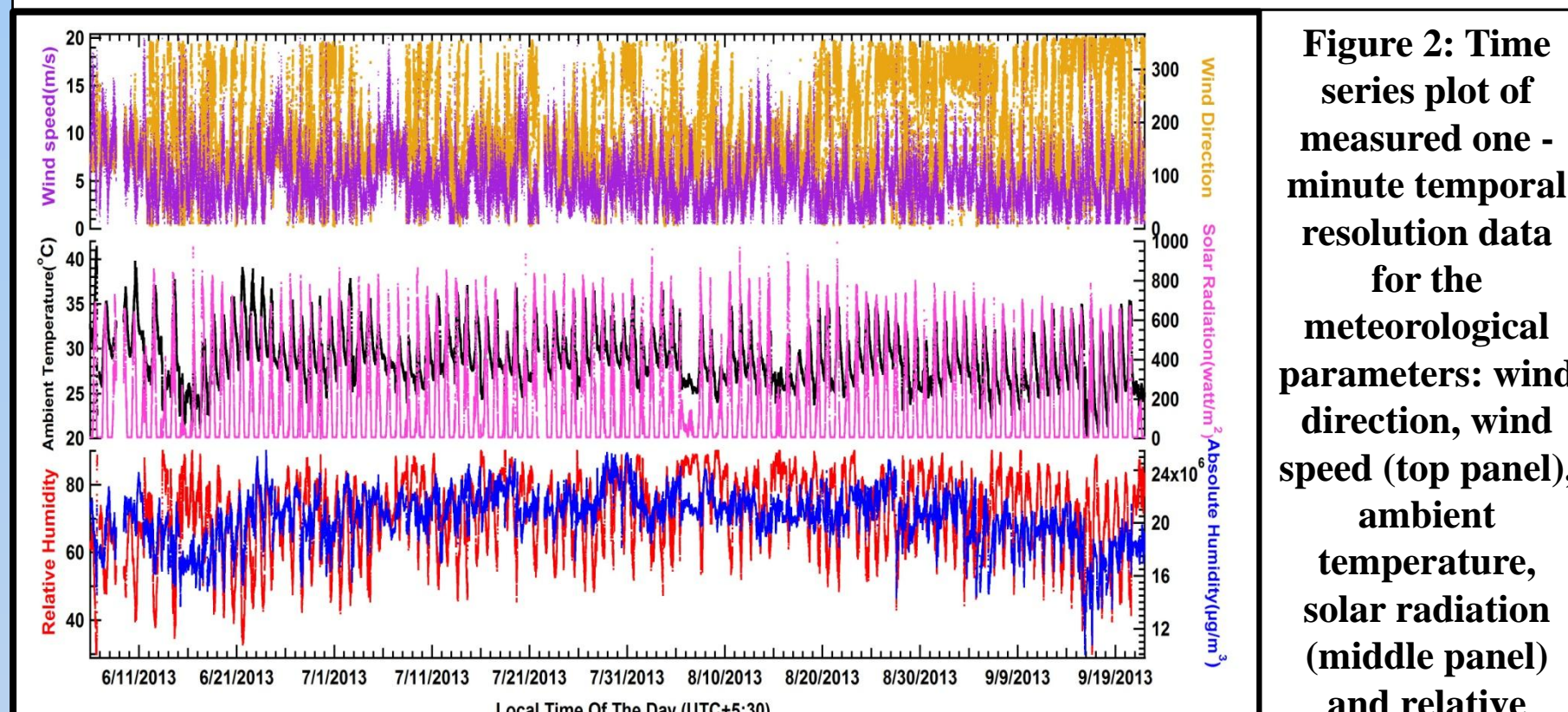
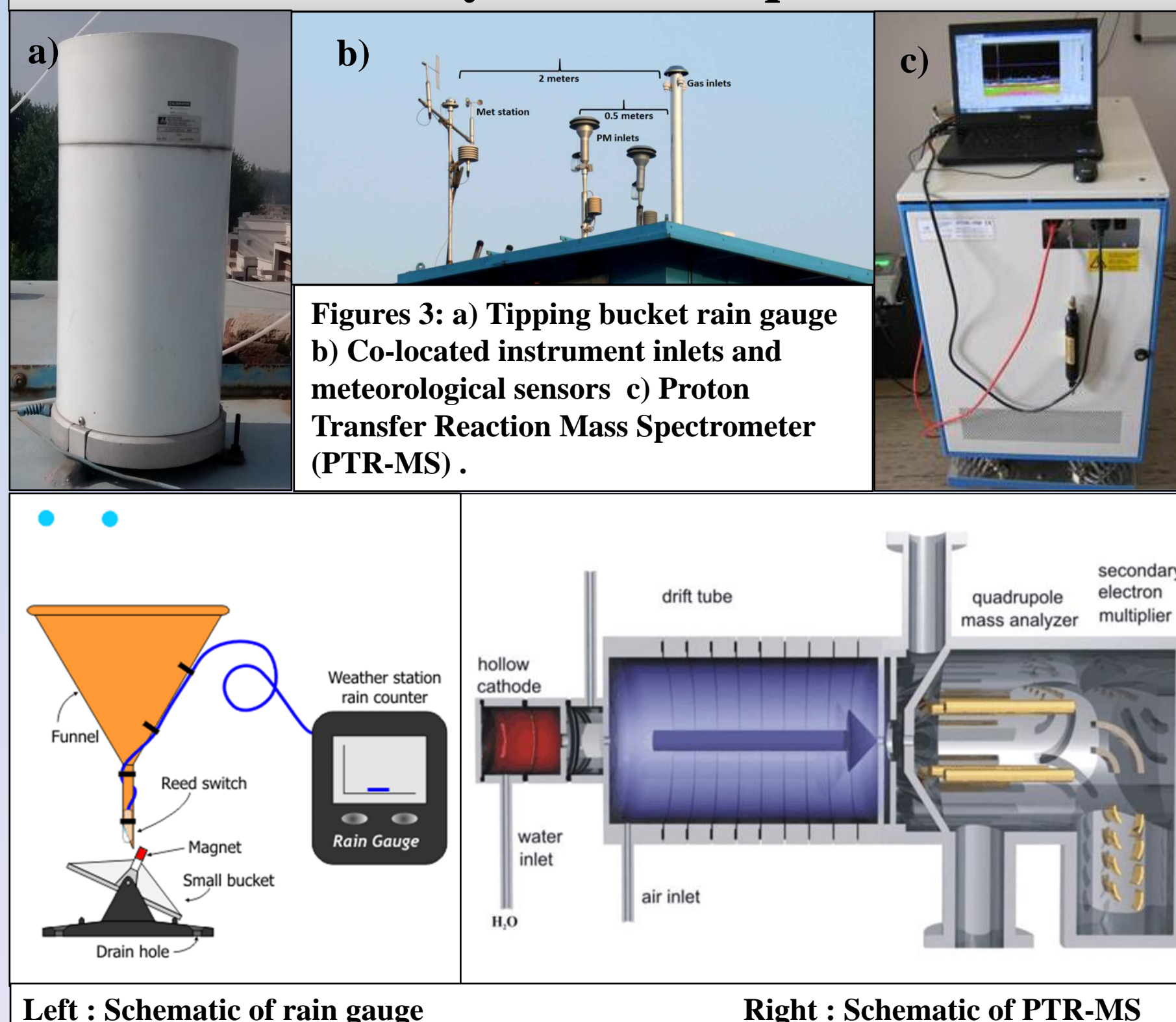


Figure 2: Time series plot of measured one-minute temporal resolution data for the meteorological parameters: wind direction, wind speed (top panel), ambient temperature, solar radiation (middle panel) and relative humidity and absolute humidity (bottom panel) during monsoon 2013.

Monsoon season is characterized by strong wind flow from south east wind sector which was present for ~54% of the season. The average ambient temperature during the season was $\sim 29^\circ\text{C}$.

Analytical techniques



Figures 3: a) Tipping bucket rain gauge b) Co-located instrument inlets and meteorological sensors c) Proton Transfer Reaction Mass Spectrometer (PTR-MS).

Left: Schematic of rain gauge Right: Schematic of PTR-MS

Proton Transfer Reaction Mass Spectrometry (PTR-MS)

- Ion source: Production of highly pure ($95\% - 99\%$) H_3O^+ ion.
- Drift tube: Non-dissociative proton transfer from H_3O^+ to VOCs.
- Analyzing system: Mass separation and detection of ions.

Table 1: Characterization of Quadrupole PTR-MS Sensitivity.

VOC	Nominal protonated (m/z)	Sensitivity (ncps/ppbv)	Limit of detection (ppbv)	Uncertainty
Methanol	33	11.6	1.04	12.3 %
Acetonitrile	42	13.6	0.03	13 %
Acetaldehyde	45	16.1	0.17	13 %
Acetone	59	18.7	0.15	10 %
Isoprene	69	8.6	0.12	17 %
Benzene	79	11.8	0.05	11 %
Toluene	93	12.7	0.13	8.6 %
P-Xylene	107	10.8	0.10	11 %
1,2,4-Trimethylbenzene	121	9.4	0.06	16 %

Results and discussion

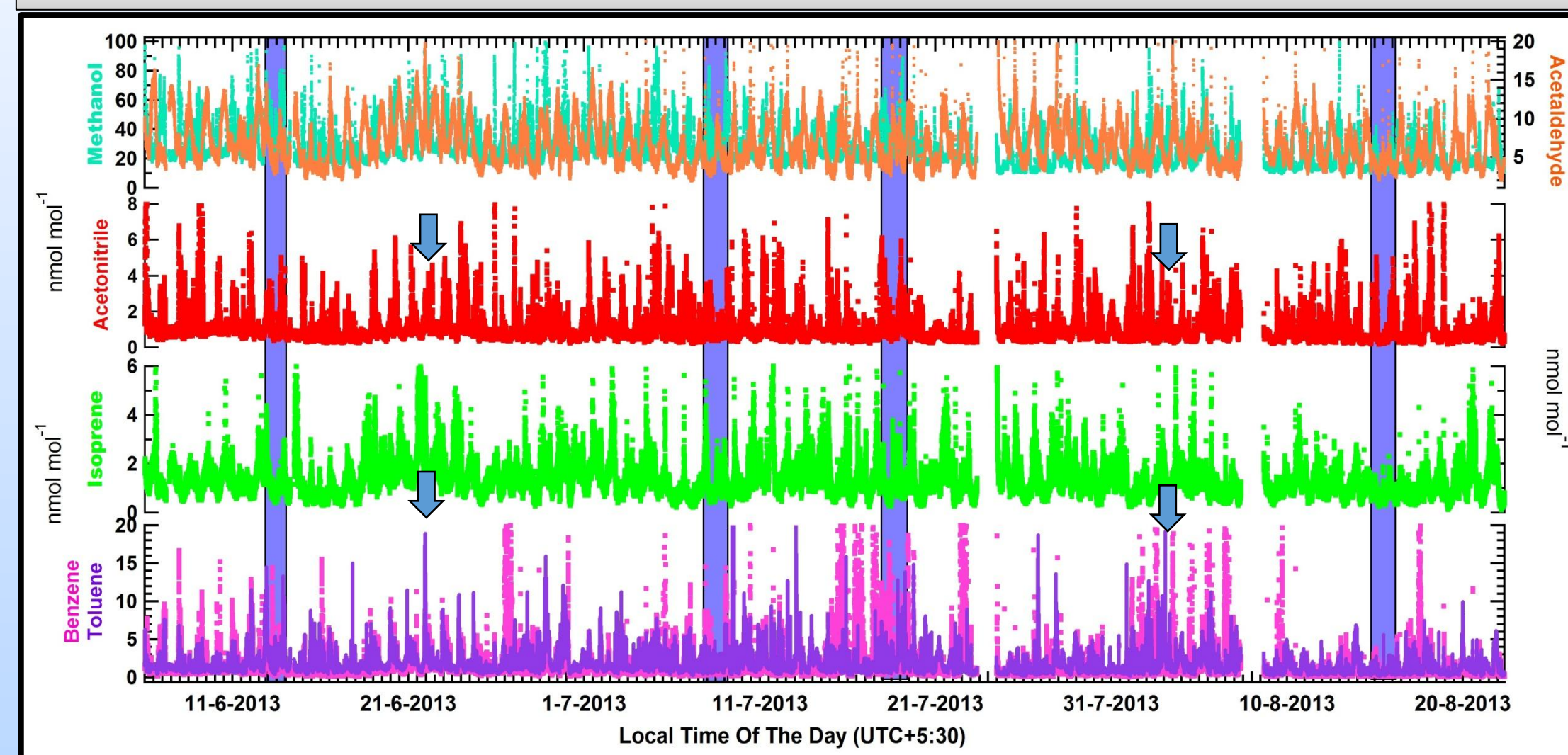


Figure 4: Time series of the one-minute data during monsoon 2013 for the mixing ratios of methanol, acetaldehyde (top panel), acetonitrile (2nd panel), isoprene (3rd panel) and benzene, toluene (bottom panel). The shaded region indicates selected rain events and the arrow mark indicates selected plume events.

The measured average \pm standard deviation for mixing ratios of the compounds for the entire season were: methanol ($25.4 \pm 11.5\text{ nmol mol}^{-1}$) > acetone ($8.8 \pm 7.1\text{ nmol mol}^{-1}$) > acetaldehyde ($6.8 \pm 4\text{ nmol mol}^{-1}$) > toluene ($1.8 \pm 1.5\text{ nmol mol}^{-1}$) > benzene ($1.6 \pm 3.2\text{ nmol mol}^{-1}$) > isoprene ($1.4 \pm 1.0\text{ nmol mol}^{-1}$) > acetonitrile ($1 \pm 0.9\text{ nmol mol}^{-1}$) > sum of xylenes ($0.8 \pm 0.8\text{ nmol mol}^{-1}$) > sum of trimethyl benzenes ($0.6 \pm 0.5\text{ nmol mol}^{-1}$).

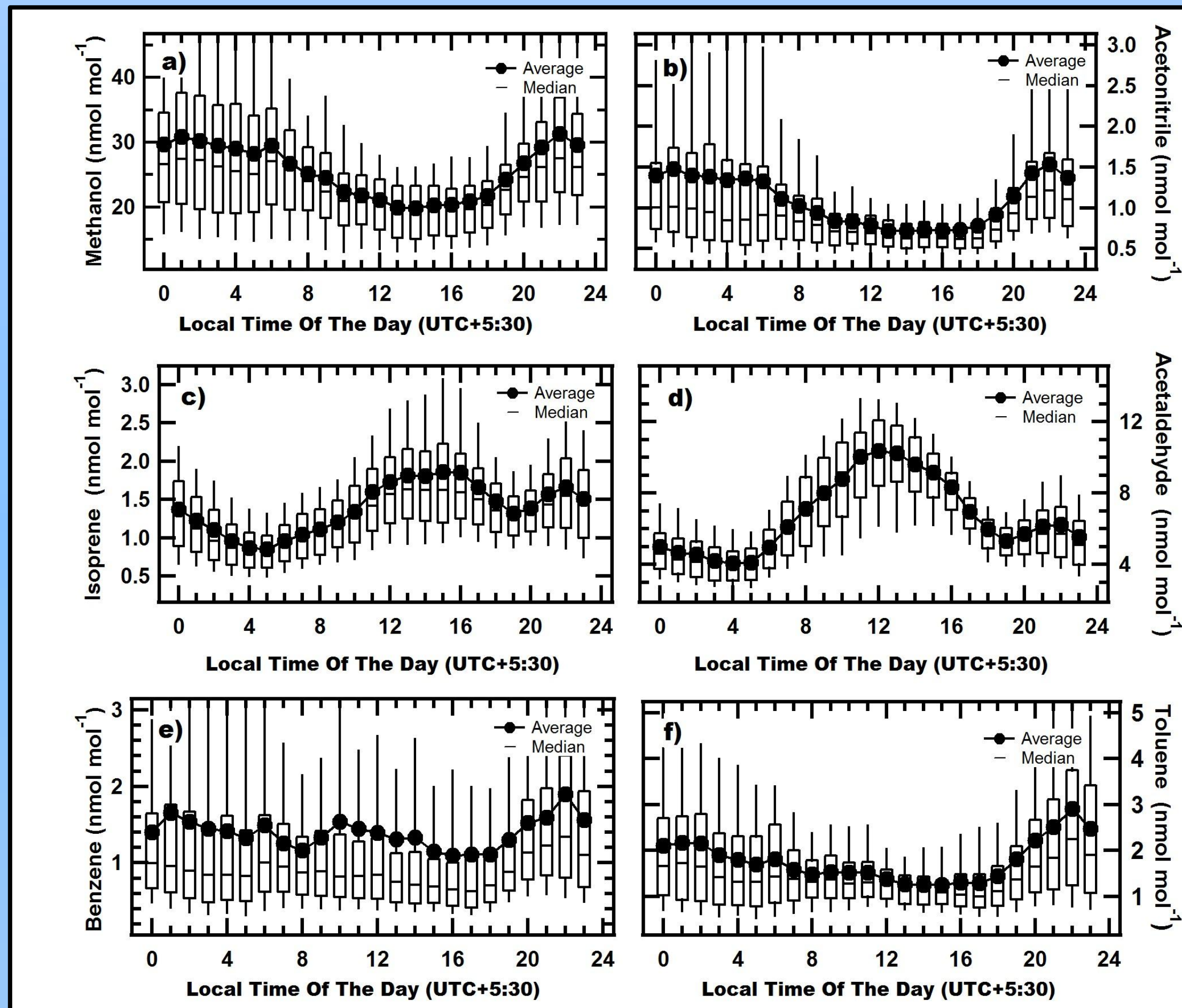


Figure 5: Diel box whisker plot of (a) methanol (b) acetonitrile (c) isoprene (d) acetaldehyde (e) benzene (f) toluene for monsoon season of 2013 at the measurement site.

The hourly average values during monsoon 2013 ranged between 18 nmol mol^{-1} to 31 nmol mol^{-1} for methanol, 0.7 nmol mol^{-1} to 1.6 for acetonitrile, 7 nmol mol^{-1} to 11 nmol mol^{-1} for acetone, 5 nmol mol^{-1} to $10.5\text{ nmol mol}^{-1}$ for acetaldehyde, 1.2 nmol mol^{-1} to 2.4 nmol mol^{-1} for benzene, 1.2 nmol mol^{-1} to 2.9 nmol mol^{-1} for toluene, 0.5 nmol mol^{-1} to 1.8 nmol mol^{-1} for C8-aromatics (sum of xylenes), 0.4 nmol mol^{-1} to 1.2 nmol mol^{-1} for C9-aromatics (sum of trimethyl benzene isomers) and 0.8 nmol mol^{-1} to 1.9 nmol mol^{-1} for isoprene.

A diurnal cycle in mixing ratios was noticeable with daytime maxima for acetaldehyde ($10.1\text{ nmol mol}^{-1}$, 12:00-13:00) and isoprene (1.9 nmol mol^{-1} , 13:00-14:00).

Selected plume events

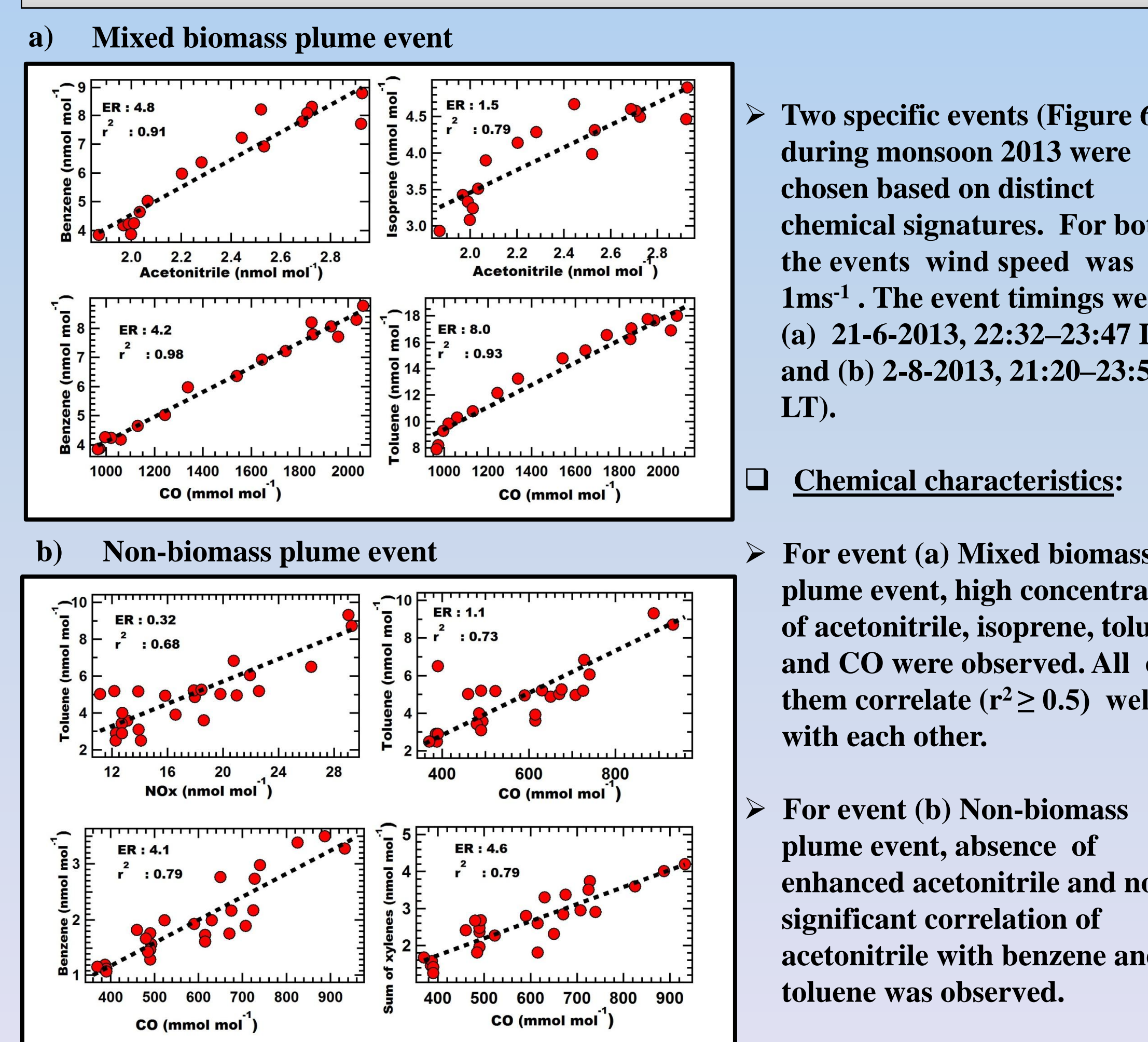


Figure 6: Correlation plots for the selected events (a) Mixed biomass plume event (b) Non-biomass plume event observed at the measurement site during monsoon 2013.

Calculating the scavenging efficiency of monsoon rain for different volatile organic compounds

C_x - Mixing ratio of x in nmol mol^{-1} ; ML - Mixed Layer Height

For correction of rain event mixing ratios due to ML:

$$\text{Corrected rain (x)} = C_x \times (\text{ML dry} / \text{ML rain})$$

Definition of scavenging ratio:

$$\text{Scavenging ratio (x)} = \text{dry } (C_x) / \text{Corrected rain } (C_x)$$

For comparing the ambient levels of VOCs during a rain event and a non rain event the data acquired from PTR-MS was divided into two categories namely rain event ($n > 3500$) and dry conditions ($n > 100,000$) based on the rainfall data.

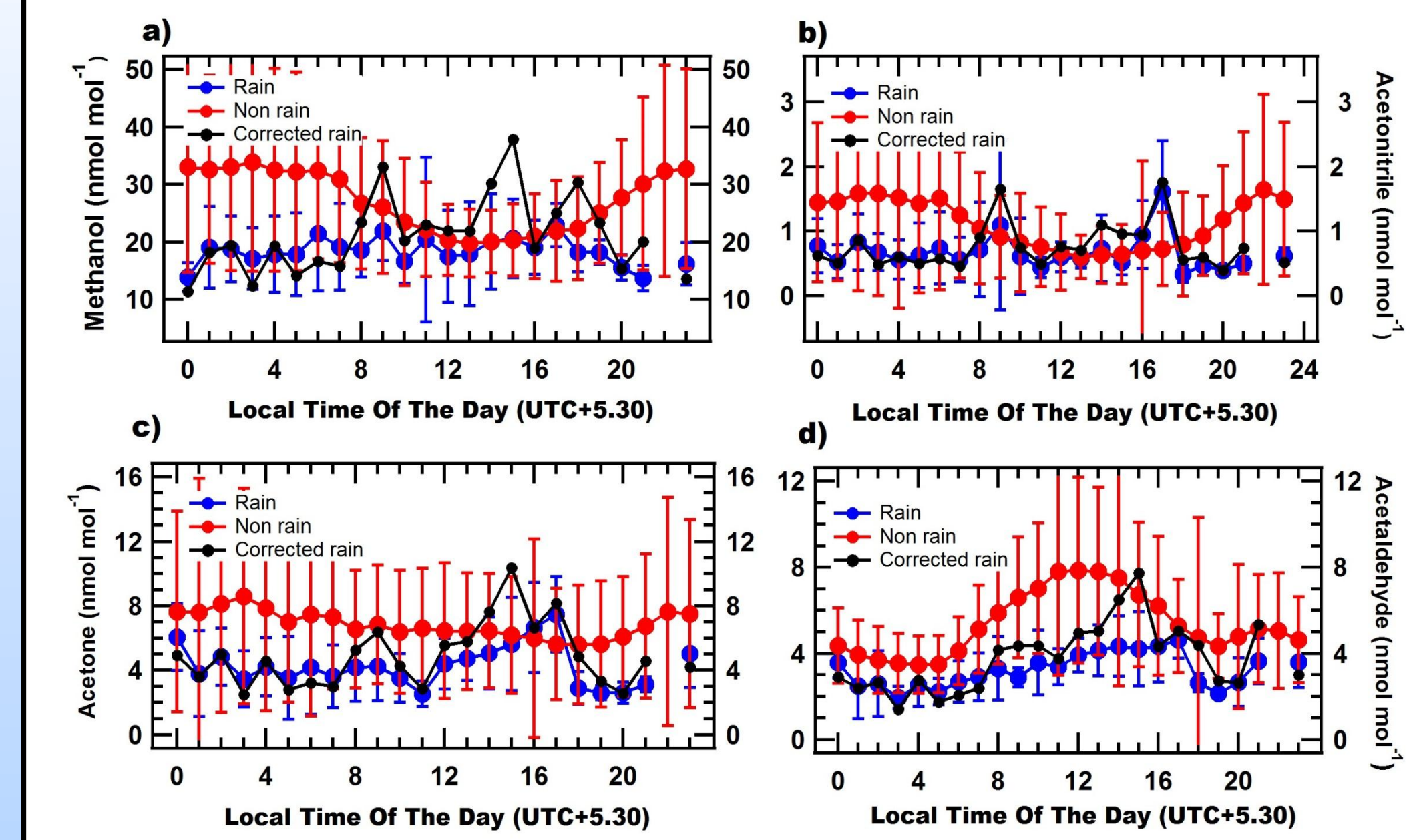


Figure 7: Average diel variability plot of (a) methanol (b) acetonitrile (c) acetone (d) acetaldehyde along with the mixed layer corrected profile (black marker) filtered for South East ($90^\circ - 180^\circ$) direction.

Factors which can contribute to difference in concentration of VOCs between rain events and dry conditions

Emissions/Fetch region (Wind direction)

a) Dry conditions b) Rain events

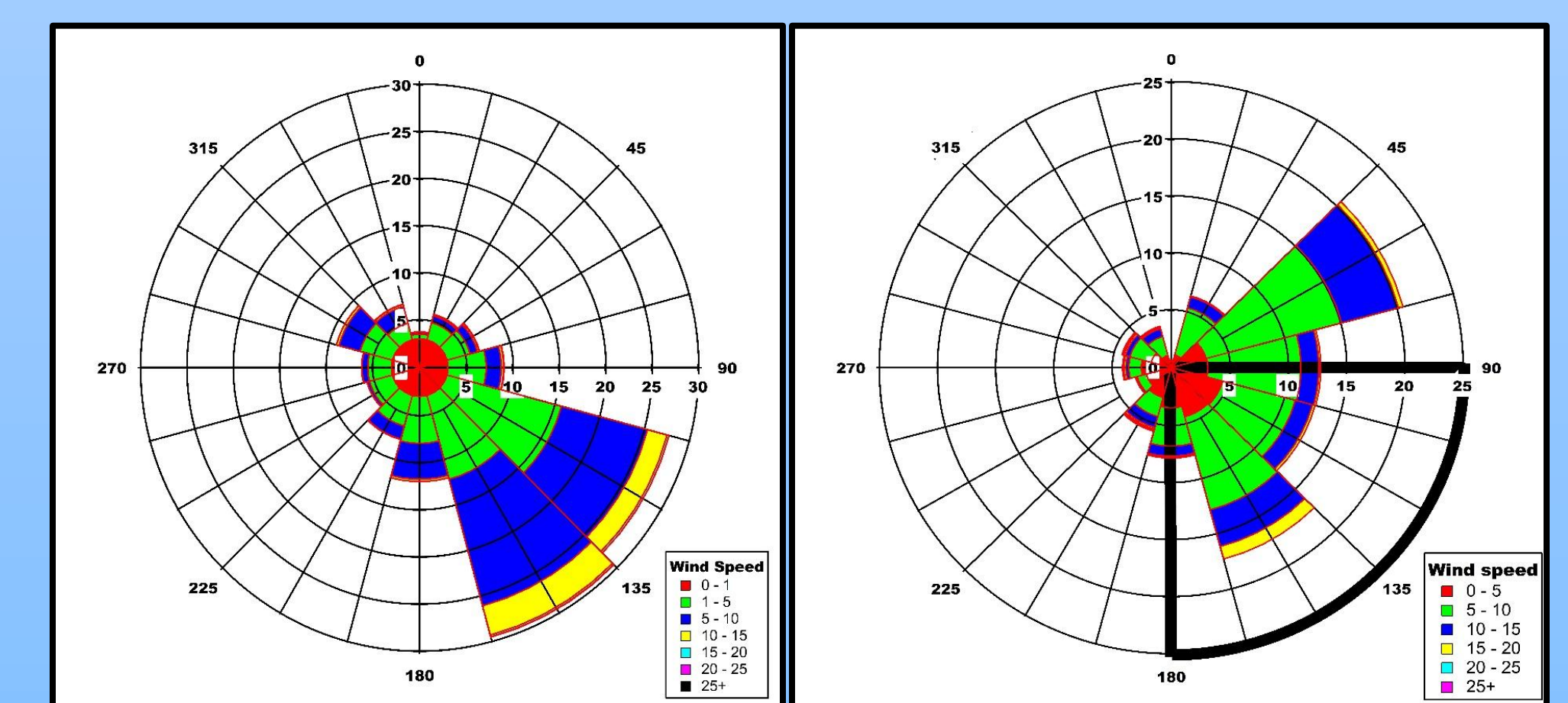


Figure 8: Rose plot derived from in situ one minute wind direction and wind speed data at the measurement site (30.667°N , 76.729°E , 310 m a.s.l.) during (a) rain events and (b) dry conditions of monsoon 2013 respectively.

Solar radiation (can act as photochemical source/sink of VOCs).

Mixed layer height (affects conversion of emission to concentration).

Derived wet scavenging efficiency of VOC in relation to their solubility for night time

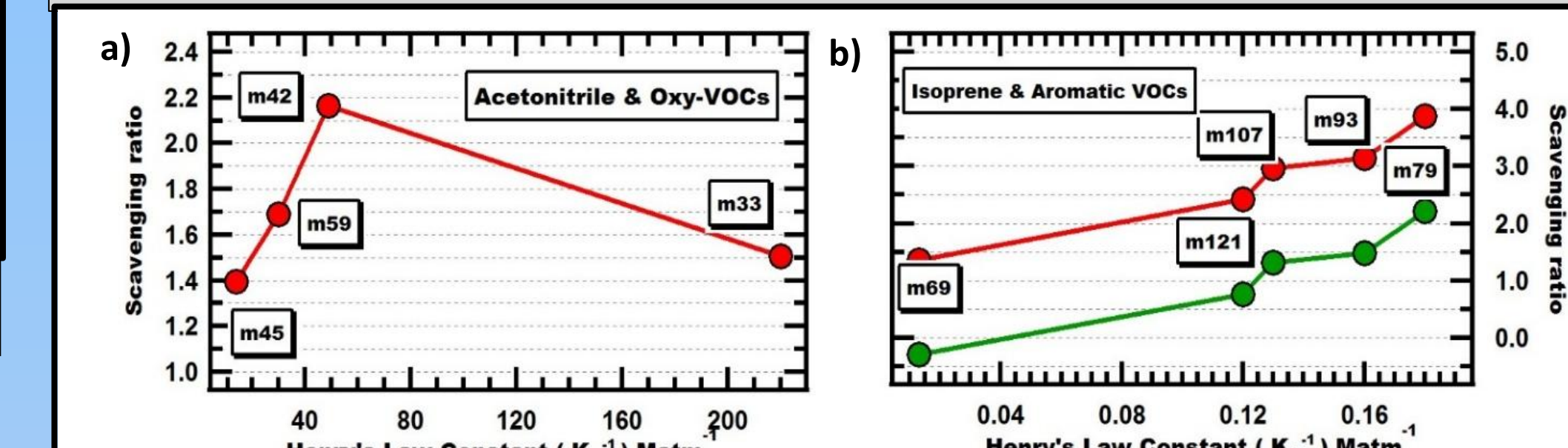


Figure 9: Plot of wet scavenging efficiency of monsoon rain against the Henry's law constant for (a) methanol (m33), acetonitrile (m42), acetone (m59), acetaldehyde (m45) and (b) benzene (m79), toluene (m93), sum of xylene (m107), sum of trimethyl benzene (m121) and isoprene (m69) during night time (18:00 - 23:00) along with the CO corrected profile (green marker).

High values of scavenging ratios are observed for aromatics during nighttime due to increased emissions activities such as burning which elevates the difference between dry and wet concentrations of VOCs. Therefore the night time scavenging ratios of VOCs are corrected using scavenging ratio of CO.

Wet scavenging ratios of all VOCs (except methanol) agree with the solubility trend.

The observed trend in wet scavenging efficiency was: acetonitrile > methanol > acetone > acetaldehyde for oxygenated VOCs and benzene > toluene > sum of xylenes > trimethyl benzene for aromatic VOCs and olefins.

The likely explanation for the anomalous behavior of methanol is that even in the absence of rain events, the presence of humid conditions contribute significantly to the removal of methanol, which is highly soluble thus reducing contribution to removal due to rains.

Conclusion

- This study is the first ever to deploy a proton transfer reaction mass spectrometer (PTR-MS) for measurements of a suite of volatile organic compounds during the monsoon season in India.
- Using inter-VOC correlation analysis for groups of VOCs with acetonitrile NO_x and CO, we found that even in monsoon season biomass burning is an active emission source.
- The wet scavenging efficiency of VOCs are influenced by several factors and solubility is just one of them.
- Photochemistry appears to mask solubility driven wet scavenging efficiency as suggested by daytime data (data not shown).
- Care should be taken while using Henry's law constant (solubility) as a proxy for wet scavenging in models as this can lead to large errors.

Acknowledgement

We acknowledge IISER Mohali Atmospheric chemistry facility and Ministry of Human Resource and Development (MHRD), India for support and funding. Haseeb Hakim acknowledges DST-INSPIRE fellowship.

References

- Sinha, V., Kumar, V., and Sarkar, C.: Chemical composition of pre-monsoon air in the Indo-Gangetic Plain measured using a new PTR-MS and air quality facility: high surface ozone and strong influence of biomass burning, *Atmos. Chem. Phys.*, 14, 5921-5941, 2014.
- Sander, R.: Compilation of Henry's law constants, version 3.99, *Atmos. Chem. Phys. Discuss.*, 14, 29615-30521, doi:10.5194/acpd-14-29615-2014, 2014.
- Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model, access via NOAA ARL READY Website - <http://ready.arl.noaa.gov/HYSPLIT.php>, NOAA Air Resources Laboratory, Silver Spring, 2013.