

# **Wet Scavenging Efficiency of Volatile Organic Compounds in the N.W. IGP**

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*A dissertation submitted for the partial fulfilment of  
BS-MS dual degree in Science*



**Indian Institute of Science Education and Research Mohali  
April 2015**



# Certificate of Examination

This is to certify that the dissertation entitled “Wet Scavenging Efficiency of Volatile Organic Compounds in the N.W. IGP” submitted by Mr. Haseeb Hakkim (MS10081) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. V. Sinha  
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Dated: April 24, 2015



# Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Vinayak Sinha at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Haseeb Hakkim  
(Candidate)

Dated: April 24, 2015

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Vinayak Sinha  
(Supervisor)



# Acknowledgment

I acknowledge the IISER Mohali Atmospheric Chemistry Facility, Ministry of Human Resource Development for support and funding. H.H acknowledges the DST INSPIRE fellowship.

I thank the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model used in this study. We thank the ESA Glob Cover 2009 Project (ESA 2010 and UC Louvain) for providing a high-resolution land classification map of the region.

I would like to express my gratitude to Dr. Vinayak Sinha, my project supervisor for his kind supervision and guidance in completing my dissertation. I am indebted for his continuous patient guidance, support, enthusiasm, feedback and suggestions, which motivated me to learn more and work harder towards the project.

I am thankful to Dr. Bärbel Sinha for providing the valuable inputs. Her support and inspiring suggestions have been precious for the development of this thesis content . I also appreciate my lab members Vinod Kumar, Chinmoy Sarkar, Saryu Garg, B. Prafulla Chandra, Harshita Pawar, Gaurav Sharma and Savita Dutta for their assistance.

On a more personal note I would like to thank all my friends at IISER Mohali and outside especially Akhil, Ashish, Nishant, Sekhar, Arul, TJ, Anubhuti and my amazing 7th floor mates for never letting me doubt myself and being there whenever I needed a friend.

Finally my deepest gratitude goes to my family, my parents Abdul Hakkim and Noorjahan , my sister Sayana Hakkim and my brother-in-law Nihas Basheer for making me live the most unique, magic and carefree childhood that has made me who I am. They bore me, raised me, supported me, taught me, and loved me throughout my life . To them I dedicate this thesis.





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# Notation (Abbreviations)

1. PTR-MS Proton-transfer-reaction mass spectrometer
2. VOC Volatile organic compound
3. HYSPLIT Hybrid single particle lagrangian integrated trajectory
4. ML Mixed layer depth
5. NOAA National Oceanic and Atmospheric Administration
6. OVOC Oxygenated volatile organic compound





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# Abstract

Volatile Organic compounds (VOCs) are important as they play a major role in the oxidation chemistry of the atmosphere leading to the formation of atmospheric pollutants such as ozone and secondary organic aerosols. Moreover certain VOCs such as benzene and formaldehyde have direct health impacts. 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 over any Indian site during the monsoon season from June- September 2013 in Mohali (30.667<sup>0</sup>N; 76.729<sup>0</sup>E; N.W. IGP). 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 ( $0.6 \pm 0.5 \text{ nmol mol}^{-1}$ ). The average mixing ratios of these VOCs were intercompared with summertime measurements from the same site conducted earlier in the year. The measured average  $\pm$  standard deviation for mixing ratios during summer 2013 were : methanol ( $44.9 \pm 25.6 \text{ nmol mol}^{-1}$ ) > acetone ( $9.3 \pm 12.9 \text{ nmol mol}^{-1}$ ) > acetaldehyde ( $7.3 \pm 3.9 \text{ nmol mol}^{-1}$ ) > toluene ( $2.5 \pm 2.5 \text{ nmol mol}^{-1}$ ) > benzene ( $1.6 \pm 1.5 \text{ nmol mol}^{-1}$ ) > isoprene ( $1.6 \pm 0.8 \text{ nmol mol}^{-1}$ ) > acetonitrile ( $0.97 \pm 0.8 \text{ nmol mol}^{-1}$ ) > sum of xylenes ( $1.9 \pm 1.8 \text{ nmol mol}^{-1}$ ) > sum of trimethyl benzenes ( $0.9 \pm 1 \text{ nmol mol}^{-1}$ ) One of the major factors responsible for the lower mixing ratios during monsoon and the summer season was the enhanced wet scavenging efficiency of VOCs during the monsoon. This was further investigated by elucidating individual factors governing the concentration of the species in monsoon season. In the case of a rain event, soluble species that exist below clouds dissolve into falling raindrops and are

removed from the atmosphere depending on the rain event characteristics (rain intensity, raindrop size) and the species' physical and chemical properties. A high sensitivity proton transfer reaction quadrupole mass spectrometer (PTR-QMS), was used to quantify VOCs during periods when it rained and when it was dry. The collective impact of boundary layer dilution, photochemistry and change in emission sources on the ambient concentrations of the VOCs were delineated using meteorological measurements to obtain the first field dataset derived wet scavenging ratios for the compounds. It was found that the values and trend in wet scavenging ratios for oxygenated VOCs and acetonitrile were: acetonitrile (2.87) > methanol (2.35) > acetone (2.26) > acetaldehyde (1.49) whereas for aromatics VOCs and isoprene it was: benzene (5.75) > toluene (5.73) > sum of xylenes (5.42) > trimethyl benzene (4.22) > isoprene (1.41). These results show that while solubility is a good proxy for parameterizing wet scavenging efficiency in atmospheric chemistry and transport models, simple use of solubility as a proxy would lead to large errors for compounds like methanol and other oxygenated VOCs in the daytime. Instead, the experimentally determined wet scavenging ratios from ambient field studies as showcased here would be a better way forward for parametrizing wet scavenging in atmospheric models.

# Chapter 1

## Introduction

The United States Environmental Protection Agency (EPA) considers a VOC as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions (EPA [www.epa.gov](http://www.epa.gov)). Health Canada classifies VOCs as organic compounds having high vapour pressure ( $> 0.01\text{kPa}$  at  $250\text{ C}$ ) and low boiling point ( $50\text{ }^{\circ}\text{C}$  to  $260\text{ }^{\circ}\text{C}$ ) measured at a standard atmospheric pressure of  $101.3\text{ kPa}$  (HC [www.hc-sc.gc.ca](http://www.hc-sc.gc.ca)). VOCs are emitted from a wide variety of both biogenic and anthropogenic sources. Biogenic sources include terrestrial plants, water bodies, soil, sediments, decomposition of organic materials and hydrocarbon reservoirs etc<sup>1</sup>. The major anthropogenic sources are motor fossil fuel burning, chemical manufacturing facilities, refineries, factories and biological process like livestock husbandry, landfills etc<sup>2</sup>. Globally the biogenic source ( $\sim 1300\text{ TgC}$ , Guenther et al., 2006,  $1\text{Tg C} = 10^{12}\text{ g C}$ )<sup>3</sup> of VOCs outnumbers the anthropogenic sources ( $\sim 150\text{ TgC}$ , Müller, 1992, Fuentes et al., 2000)<sup>4, 5</sup>. 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. carcinogenic benzene)<sup>6</sup>.

Wet scavenging is a very important cleansing mechanism of the atmosphere, especially for trace VOCs and yet it is poorly understood. When it rains the water droplets dissolve and scavenges atmospheric gaseous molecules as well as aerosol particles from the atmosphere that contains a large variety of inorganic and organic trace gases<sup>7</sup>. There have been several

studies that have focused on VOCs in rainwater<sup>8</sup>. In most of the previous studies focused on scavenging efficiencies, the species studies were radioactive particles, sea salt, non-sea salt sulfate, nitrate, methane sulfonate, sodium, sulfur dioxide, particulate matter, carbonaceous aerosols, trace metals, polycyclic aromatic hydrocarbons(PAHs), and mercury (Barrie,1985; Engelmann, 1971; Duce et al., 1991; Galloway et al., 1993; Guentzel et al., 1995; Franz and Eisenreich, 1998; Sakata and Asakura, 2007; He and Balasubramanian, 2009; Rothenberg et al., 2010; Hegg et al., 2011; Škrdlíková et al., 2011)<sup>9</sup>. There are also various studies which reported the scavenging of atmospheric organic contaminants including polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) by snow.<sup>10</sup> On the other hand due to analytical challenges associated with measurements of reactive VOCs which are present only at ppt-ppb concentrations in the troposphere, to the best of our knowledge no experimental studies reporting the wet scavenging efficiencies of compounds such as methanol, acetone, acetaldehyde, isoprene, benzene, toluene and xylenes exist. Wet deposition depends on the amount, type and intensity of the precipitation and on the properties of the scavenged material, including whether it is in particulate or gaseous form. The removal of gaseous compounds is mainly based on physical (condensation, adsorption and absorption) and chemical processes in the droplet and at the droplet's surface<sup>11</sup>. When a gas is in high concentration in the atmosphere and at very low concentration in water droplet, there is a transfer of the compound from the gas phase to the aqueous phase<sup>12</sup>. One of the main factors which affect these wet removal processes is solubility of the gas and gaseous wet scavenging parameterizations are often based on Henry's law. Therefore in order to parameterize removal rates due to rain, solubility is the most widely used proxy in atmospheric chemistry and transport models<sup>13</sup>. Unfortunately, other processes such as aqueous phase reactions within the droplet can provide a reactive sink for the compound and interfere with this simple Henry's law based parameterization. Currently, aqueous phase reactions, in particular of more complex organic molecules, are poorly understood and rarely accounted for in models. The processes of uptake and release of gases from the cloud or rain droplets is formulated following the Henry's law equilibrium and yet experimentally this remains to be validated for VOCs, due to the challenges in measuring VOCs. As the VOCs undergo complex and often multiphase chemical processes influenced by various meteorological conditions that are present in the real world, the wet scavenging process

doesn't not always depend linearly on the solubility as simulated by climate models or measured by the laboratory experiments. Therefore real time ambient measurements are essential for the validation of models. To date there are only very few observations and analysis at high spatial and temporal resolution available for validating model performance<sup>14</sup>. The representation of wet removal processes in various global chemical transport and general circulation models have been compared in *P. J. Rasch et al* 1999 and the analysis suggests that there are systematic discrepancies between most of the model simulations and observations<sup>15</sup>. Hence experimental data is necessary to constrain the accuracy of models.

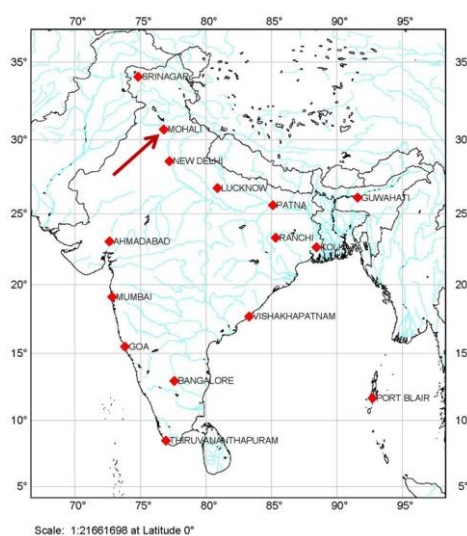
In this study, we investigated the scavenging efficiency of rainfall during the monsoon season for the following reactive volatile organic compounds: methanol, acetone, acetonitrile, isoprene, acetaldehyde, toluene, benzene, sum of xylenes and sum of trimethyl benzene. The differences in ambient concentrations of VOCs between rain events and dry periods can be influenced by many factors such as boundary layer dilution effect, photochemistry and change in fetch region for the VOC emission sources. In this study the effects of each of these factors was systematically ascertained to derive the concentration differences purely attributable to wet scavenging. Finally the experimental results are discussed with proposals for improved representation of wet scavenging in atmospheric models.

# Chapter 2

## Materials and methods

### 2.1 Site Description

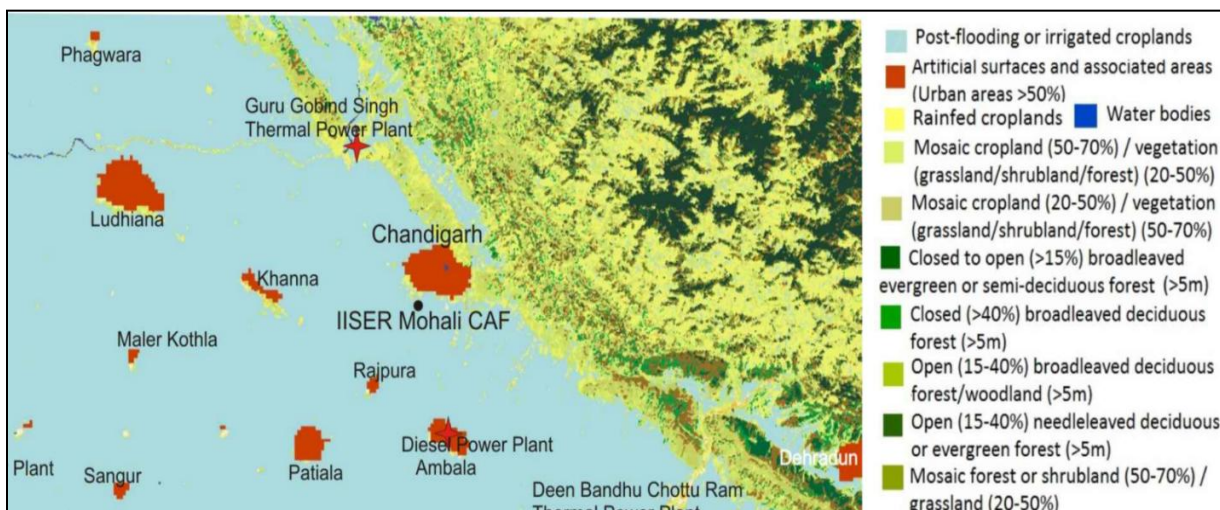
The measurement site (30.679°N, 76.729°E; 310 m a.s.l.) is a suburban area located in the north-west Indo Gangetic plain. All the measurements were performed at the IISER Mohali atmospheric chemistry facility situated in the measurement site. A detailed description of the site including technical details pertaining to sampling, inlets and instrumentation and surrounding land use are available elsewhere<sup>16</sup>. Figure 2.1 in shows the Location of the measurement site (30.6670N, 76.7290E, 310ma.s.l.) in the North West Indo-Gangetic Plain.



**Figure 2.1:** Measurement site and other major Indian cities [source: Pan Map GIS software].



Figure 2.2 shows the map of land classification in a 100km x 200km area surrounding the measurement site. In the wind sector North-East of the measurement site, lies the tricity of Mohali, Chandigarh and Panchkula. The Himalayan mountain range lies less than 30 kms away in the North West to south-east direction. This sector is classified as urban sector due to the predominant presence of urban emission sources.

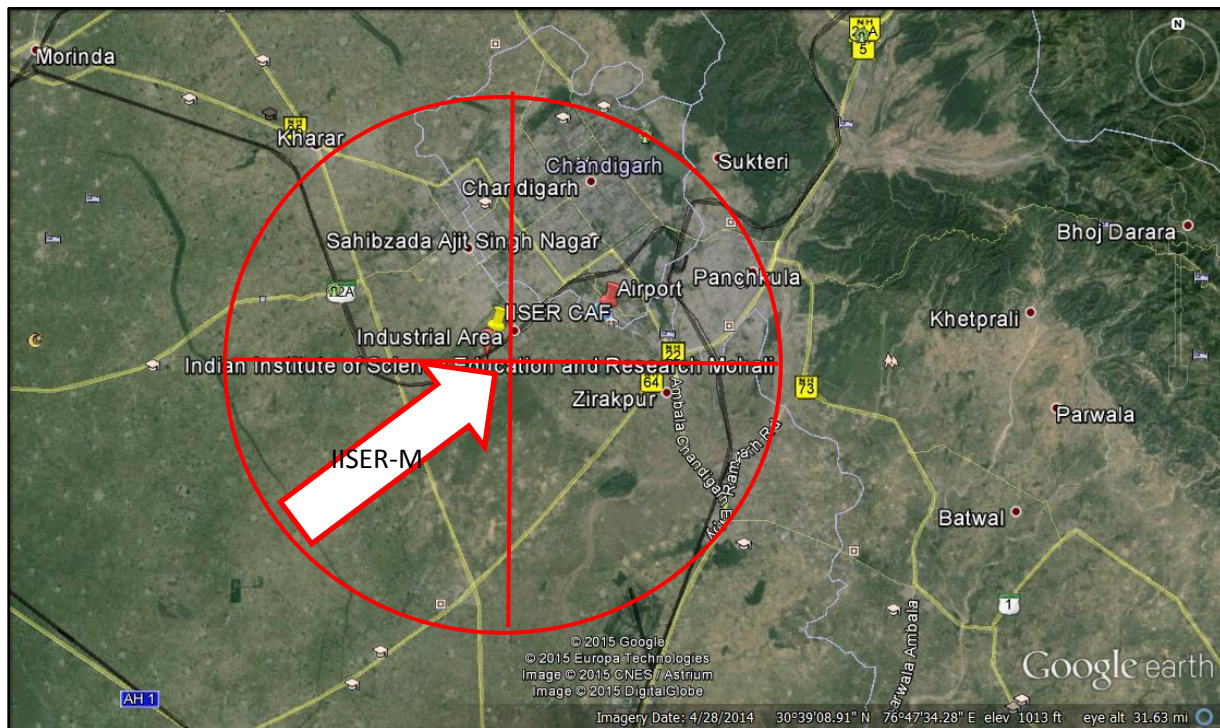


**Figure 2.2:** Map of the land use in a 100 km × 200 km area surrounding the measurement site (black dot) in the city of Mohali in the North-West Indo–Gangetic plain (30.667° N, 76.729° E, 310 m a.s.l.) (*Sinha et al., Atmos. Chem. Phys.* 2014).

The land use in the wind sector east to south (90°–180°) of the site is of a mixed type, as rural/agricultural land is interspersed with various small industries in areas such as Jagadhri (110 km from the site) and Ambala (50 km from the site). Brick kilns, glass manufacturing units, pharmaceutical industries, solvent industries and paint industries are the major small-scale industries present in this sector. The capital of India, New Delhi, lies about 300 km south of the site and the national highways (NH-1 and NH-2) that connect Delhi to northwest India also lies in this wind sector<sup>16</sup>. The wind sector spanning from South to North-West is dominated by agriculture activity, classified as rural and agricultural sector. Patiala (~60 km) and Ludhiana (~100 km) are the two major areas where industries are located. Most common small scale industries present in these areas are textile industries, dye manufacturing units and paper industries. Figure 2.3 shows the Google map image of measurement site and its surroundings.

## 2.2 General Meteorology

The meteorological parameters e.g. wind speed, wind direction, relative humidity and solar radiation were measured using the meteorological station installed on the top of the ambient air quality station. Figure 2.4 shows the 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).



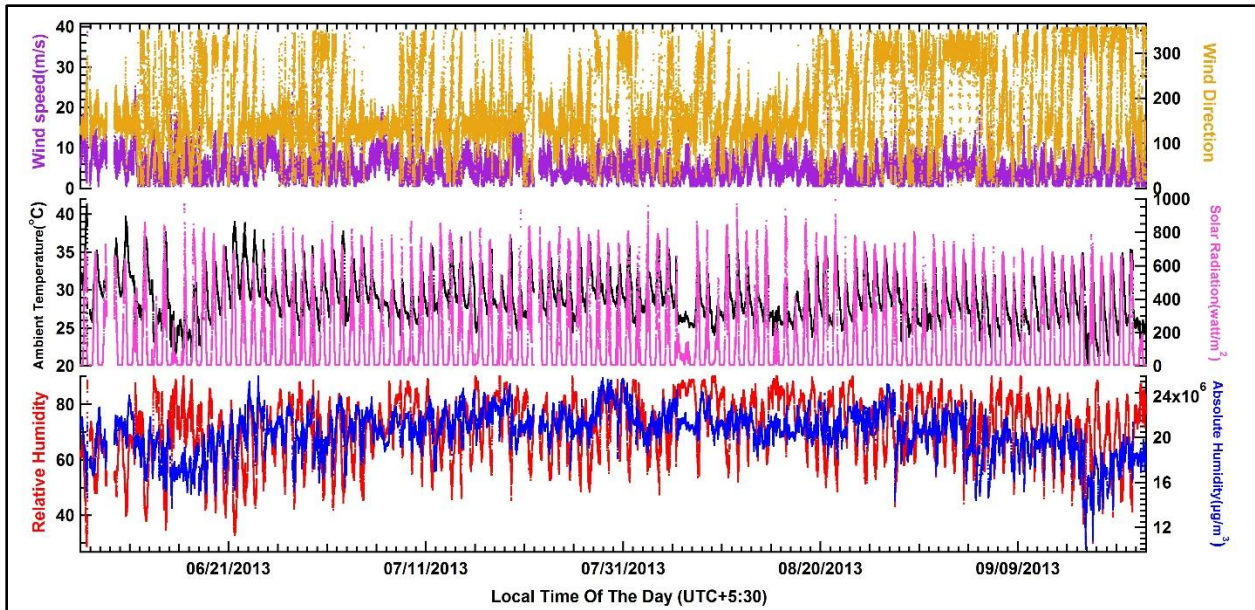
**Figure 2.3:** Google map image of measurement site and its surroundings.

During the monsoon season, the northwest Indo-Gangetic Plain is characterized by strong wind flow from south east wind sector which was present for ~54 % of the season. The wind speeds of air masses arriving from this sector typically ranged from 0.5 m/s to 25m/s with an average value of ~5.5 m/s for the entire season. The average ambient temperature was ~302 K for the period of study with a lowest value of ~293 K (9/16/2013, 2:00) and a highest value of ~314 K (6/6/2013, 15:39).

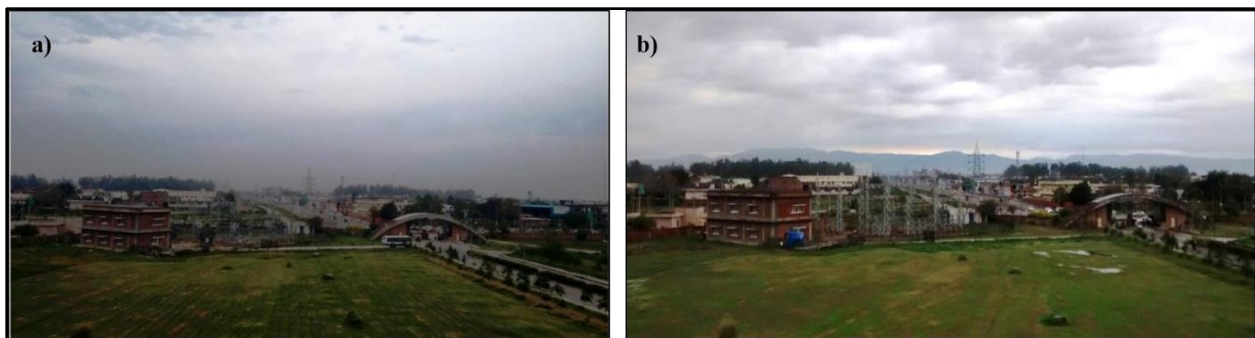
Monsoon season is interspersed with cloudy days as well as sunny days. The peak value of solar radiation ( $>900 \text{ Wm}^{-2}$ ) was observed between 12:00 and 12:59 throughout the season.



During rain events due to cloud cover less solar radiation was available with lowest value being  $1.44 \text{ Wm}^{-2}$  (6/29/2013, 14:16) . Picture 2.1 shows the view of Shivalik mountain range which is a part of the outer Himalayas from the measurement site (30.6670 N, 76.7290 E, 310m a.s.l.) during (a) dry conditions and (b) rain events.



**Figure 2.4:** 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.



**Picture 2.1:** View of Shivalik mountain range from the measurement site (30.667<sup>0</sup> N, 76.729<sup>0</sup> E, 310m a.s.l.) during dry conditions (a) and rain events (b).

## 2.3 Sampling

The amount of precipitation in millimetres and ambient concentration of following reactive volatile organic compounds: methanol, acetone, acetonitrile, isoprene, acetaldehyde, toluene, benzene, sum of xylenes and sum of trimethyl benzene were measured at ppt-ppb level and high resolution time (1 minute) for the monsoon season of 2013 starting from June 6th to September 21st. All the measurements were performed in air sampled from the IISER Mohali atmospheric chemistry facility. For the online measurement of volatile organic compounds a high-sensitivity proton transfer reaction quadrupole mass spectrometer (HS Model 11-07HS-088; Ionicon Analytik Gesellschaft, Austria) was used in the selected ion monitoring mode with a dwell time of 1 s each at the relevant m/z channels (64). The amount of precipitation was measured by means of a tipping bucket rain gauge (MODEL 370C/372C, Met One Instruments, US). Wind speed, wind direction, ambient temperature and relative humidity are measured routinely at the facility using meteorological sensors (Met One Instruments Inc., Rowlett, Texas, USA) at a temporal resolution of 1 minute. The inlets of all the instruments and the rain gauge sensor were co-located at a height of 20 m above the ground and the ambient air was drawn into each instrument through dedicated Teflon inlet tubing with inner diameter of about 3.12 mm and length less than 5 m. To avoid damage to the instrument due to blocked lines, dust particles were filtered at trace gas inlet using Teflon membrane particle filters of 5  $\mu\text{m}$  pore size. These Teflon membrane particle filters were regularly changed every week, for quality assurance. The suction flow rate for the PTR-MS instrument was 90 sccm ( standard centimetre cube per minute ). The flow rate was measured by BIOS Drycal Definer 220 flow calibrator. The inlet residence time for the PTR-MS measurements were less than 120 seconds. The inlet residence time was calculated by dividing the inner volume of the inlet tubes by the flow rate inside them. All instrumental parameters are logged daily for data quality assurance.

## 2.4 Volatile organic compound measurements using proton transfer reaction mass spectrometry (PTR-MS)

The PTR-MS detects the analyte molecule based on their mass/charge ( $m/z$ ) ratio. Within the instrument, organic compounds with proton affinity greater than water (P.A. = 165.2 kcal/mol) are chemically ionized by proton transfer with  $H_3O^+$  reagent ions and the products are detected using a quadrupole mass spectrometer<sup>17</sup>. Table 1 lists the sensitivity, detection limits and uncertainties for the ambient VOCs measured during the period of study with the  $m/z$  ratios at which they were detected. The instrument was calibrated on 11/-07/-2013 for the measured compounds (range 0.3–20 ppb) using a custom ordered VOC gas standard (Apel-Riemer Environmental, Inc., Colorado, USA; ~500 ppb for each VOC, stated uncertainty = 5%) containing compounds listed in Table 1. Sensitivity factor, limit of detection and total uncertainty of VOCs measured during study period are also given in Table 1. A complete technical description of the instrument including instrument parameters, calibration procedures and instrumental background checks has been provided previously in Sinha et al<sup>15</sup>.

**Table 1. Sensitivity factor, limit of detection and total uncertainty of VOCs measured during study period .**

VOC	Nominal protonated $m/z$ (Th)	Sensitivity (ncps ppbv <sup>-1</sup> )*	Limit of detection	Uncertainty (nmol mol <sup>-1</sup> ) <sup>^</sup>
Methanol	33	11.61	1.04	12.3%
Acetonitrile	42	13.69	0.03	13%
Acetaldehyde	45	16.05	0.17	13%
Acetone	59	18.72	0.15	10 %
Isoprene	69	8.64	0.12	17 %
Benzene	79	11.78	0.05	11 %
Toluene	93	12.65	0.13	11 %
p-xylene	107	10.80	0.10	14 %
1,2,4-Trimethylbenzene	121	9.44	0.06	16 %

\* defined as  $2\sigma$  of measured normalized signal while measuring the VOC free zero air divided by the sensitivity factor.

^root mean square propagation of 5% accuracy error in the VOC gas standard concentration, the  $2\sigma$  instrumental precision error while sampling 5-6 ppb of the benzene and flow uncertainty of 2% for each mass flow controller .

## 2.5 Rainfall measurement using a tipping bucket rain gauge

Liquid rainfall is expressed as the depth to which it would cover a horizontal projection of the earth's surface if there is no loss by evaporation, run-off or infiltration. It is expressed in terms of mm or cm<sup>14</sup>. It is assumed that the amount of precipitation collected in the gauge is representative of a certain area around the point where the measurement is made. Tipping bucket rain gauge is an accurate, sensitive meteorological device used to measure the amount of liquid precipitation over a period of time. As rain falls, it lands in the funnel of the tipping bucket rain gauge. The rainwater then travels down the funnel and drips into one of two calibrated 'buckets' balanced on a pivot. The top bucket is held in place by a magnet until it has filled to the calibrated amount (0.05mm). When the bucket has filled to this limit, the magnet will release its hold, causing the bucket to tip. When the bucket tips, it triggers a reed switch (or sensor), sending a message to the display or weather station. The display then

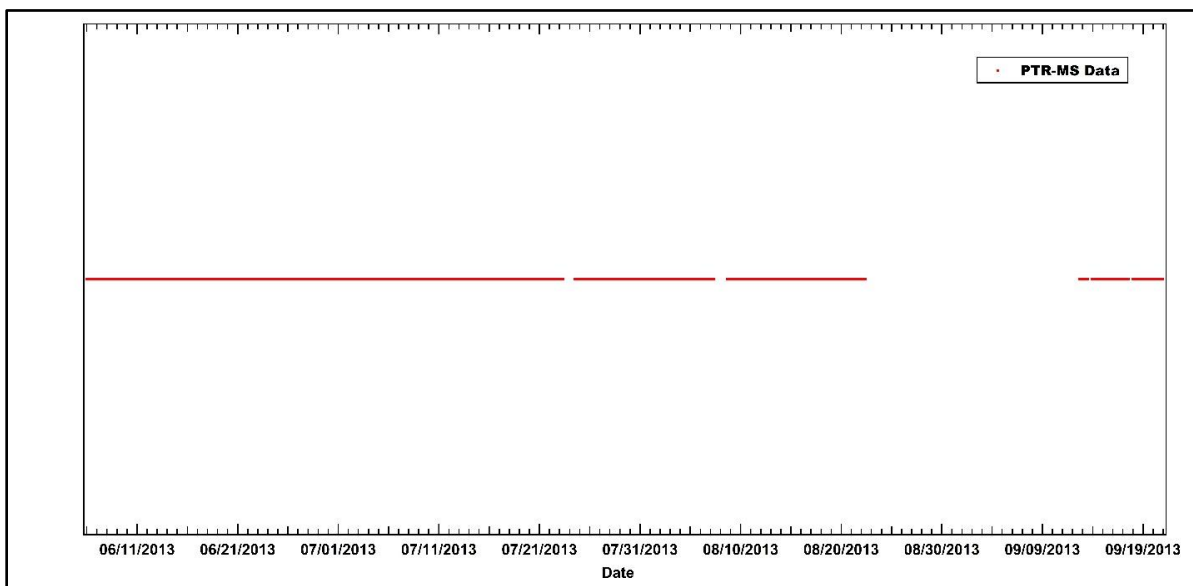


**Picture 2.2:** Picture of the tipping bucket rain gauge installed at the top of the atmospheric research facility at IISER Mohali.

counts the no of times the switch is triggered to calculate the amount of rainfall. Picture 2.2 shows the picture of the tipping bucket rain gauge (MODEL 370C/372C, Met One Instruments, US) installed at the top of the atmospheric research facility at IISER Mohali.

## 2.6 Data processing

During the period from 6/6/2013 to 22/9/2013 which is equivalent to ~156,960 min), ambient VOC data was available for 109,480 min, a data coverage of 70% of the time. Figure 2.5 shows the timeline of the ambient PTR-MS data availability between 06/06/2013 to 22/09/2013. Gaps in the data are due to preventive maintenance, calibrations and because the instrument was used for other purposes. Ten data points (02/08/13, 16:10 – 02/08/13, 16:20) which were identified as instrumental spikes during the analysis were excluded from the investigation. The ambient dataset was further subdivided as belonging to rain event or dry condition depending on the occurrence of rain or absence of rain respectively during the



**Figure 2.5:** Availability of PTR-MS data from the IISER Mohali research facility.

ambient measurements. A total of  $n > 100,000$  measurements were available for dry conditions and  $n > 3500$  measurements were available for rain events.

Rain gauge data was available for the entire monsoon season of 2013 without any gaps. The tipping bucket rain gauge has an instrumental noise of the order of 0.1 which has been accounted for in calculations of the amount of rain. The upper limit of the instrument is 24.5 mm and once it reaches the upper limit the instrument automatically resets to 0. An algorithm in IGOR PRO software was written and applied to the raw data to obtain accurate rainfall data for each rain event. Given below is the macro code used for the algorithm :

```
#pragma rtGlobals=1          // Use modern global access method.

function correct_rain(org)    //Definition of function

wave org

duplicate/O org rain_corr

rain_corr=NaN

variable i,counter

counter=0

rain_corr[0]=0

for (i=1;i<numpts(org);i=i+1)

rain_corr[i]=org[i]-org[i-1]

if (rain_corr[i]<-0.4)

rain_corr[i]=25-org[i-1]+org[i]          //to account for the rain sensor resetting at 25

//elseif (rain_corr[i]>-0.4 && rain_corr[i]<0)    //to account for fluctuation observed .

//rain_corr[i]=0

endif

endfor

rain_corr[p]=rain_corr[p]<=0.1 ? 0: rain_corr[p] //to account for instrumental noise

end
```



## **2.7 Statistical tests for assessing significance of variation in the ambient concentration of VOCs during rain events and dry conditions**

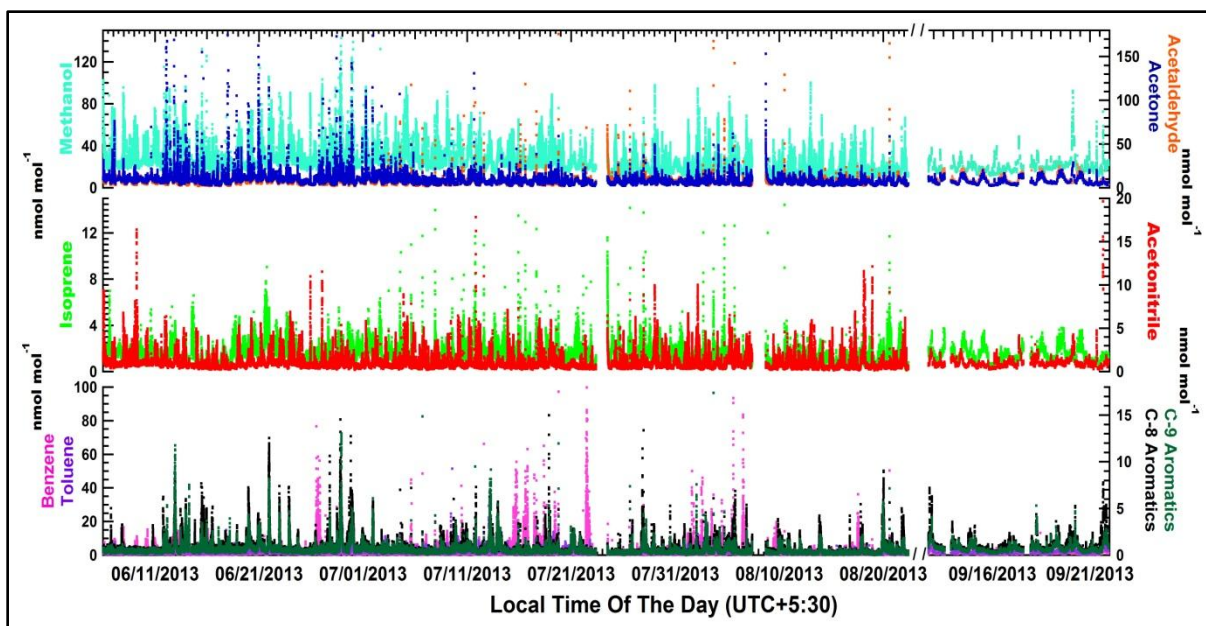
ANOVA (Analyses Of Variance) was used to determine whether the differences in VOC concentrations during rain events and dry conditions were statistically significant. The p-values were calculated for both rain event and dry condition of VOCs for every hour of a day. For all the hours in which the calculated p-values are less than  $p(0.05)$ , the variation between rain event and dry condition values are considered to be significant with a confidence interval of 95 % (2-sigma). Similarly, all the hours with a p value less than  $p(0.317)$  were considered to have a significant variation with a confidence interval of 68.3 % (1-sigma). Any hour with a significant variation less than 1-sigma was not considered for further analysis as it was considered as insignificant. The p values calculated for rain event and dry condition values of VOCs during the hours 11:00, 19:00 and 22:00 were excluded from the analysis as they are found to have significant variation with a confidence interval less than 68.3 % (1-sigma).

## Chapter 3

# Results and Discussion

### 3.1 Time series of VOC and rain data

Figure 3.1 shows the measured one-minute temporal resolution data for the mixing ratios of methanol, acetaldehyde, the sum of acetone and propanol, isoprene, acetonitrile, benzene, toluene, the sum of C8- aromatics (xylene isomers and ethyl benzene), and the sum of C9- aromatics (isomers of trimethyl benzenes and propyl benzenes). The ambient concentrations of methanol were below  $40 \text{ nmol mol}^{-1}$  for 90% of the time during the monsoon 2013. Acetonitrile concentration was below  $1.5 \text{ nmol mol}^{-1}$  for 84% of the period. The levels of acetone and acetaldehyde were below 12 for 85% and 8 for 71% of the period of study respectively. In the case of aromatics, the ambient concentration of benzene was below  $2 \text{ nmol mol}^{-1}$  and toluene was below  $2.5 \text{ nmol mol}^{-1}$  for 83% and 81% of the time respectively. The sum of xylene isomers and sum of trimethyl benzene isomers have concentrations below  $1.5$  and  $1 \text{ nmol mol}^{-1}$  for 90 and 88 % of the period of study respectively. For all these compounds, the observed concentrations were considerably lower than the concentrations measured at the same site in May 2012 (Sinha et al., 2014). Average levels of VOCs reported in sinha et.al 2014 for May 2012 ranged from  $1.2$  to  $2.7 \text{ nmol mol}^{-1}$  for aromatic VOCs,  $5.9$  to  $37.5 \text{ nmol mol}^{-1}$  for the oxygenated VOCs,  $1.4 \text{ nmol mol}^{-1}$  for acetonitrile,  $1.9 \text{ nmol mol}^{-1}$  for isoprene. The average levels of aforementioned VOCS during monsoon 2013 ranged from  $0.6$  to  $1.8 \text{ nmol mol}^{-1}$  for aromatic VOCs,  $6.8$  to  $25.4 \text{ nmol mol}^{-1}$  for the oxygenated VOCs,  $1.1 \text{ nmol mol}^{-1}$  for acetonitrile,  $1.4 \text{ nmol mol}^{-1}$  for isoprene. The lower concentrations in monsoon season despite the fact that the fetch region is the more densely

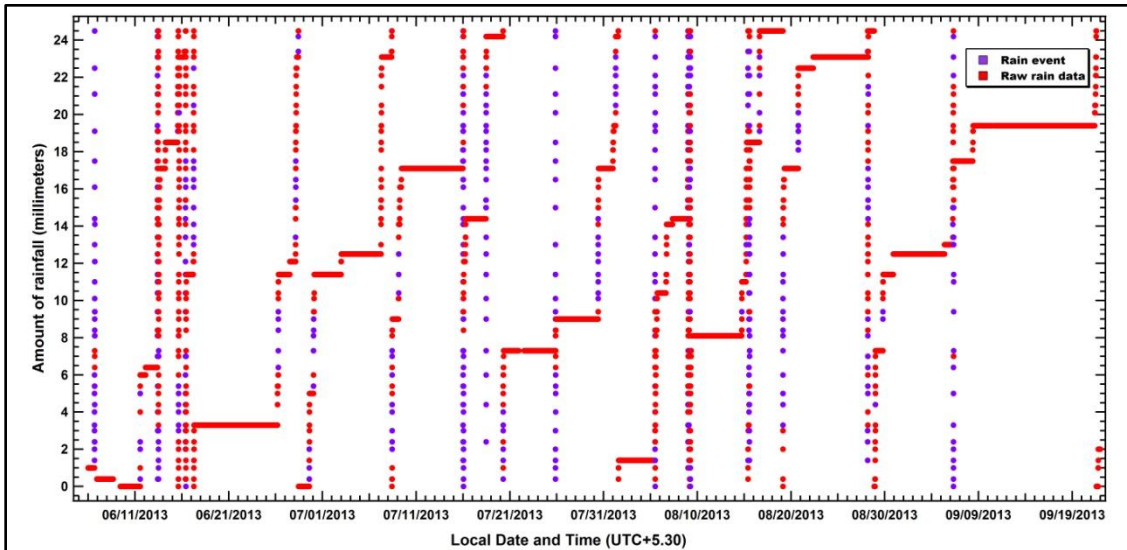


**Figure 3.1:** Time series plot of measured one-minute temporal resolution data for the mixing ratios of methanol, acetaldehyde, the sum of acetone and propanol (top panel), isoprene and acetonitrile (middle panel) and benzene, toluene, the sum of C8- aromatics (xylene isomers and ethyl benzene), and the sum of C9-aromatics (isomers of trimethyl benzenes and propyl benzenes) (bottom panel).

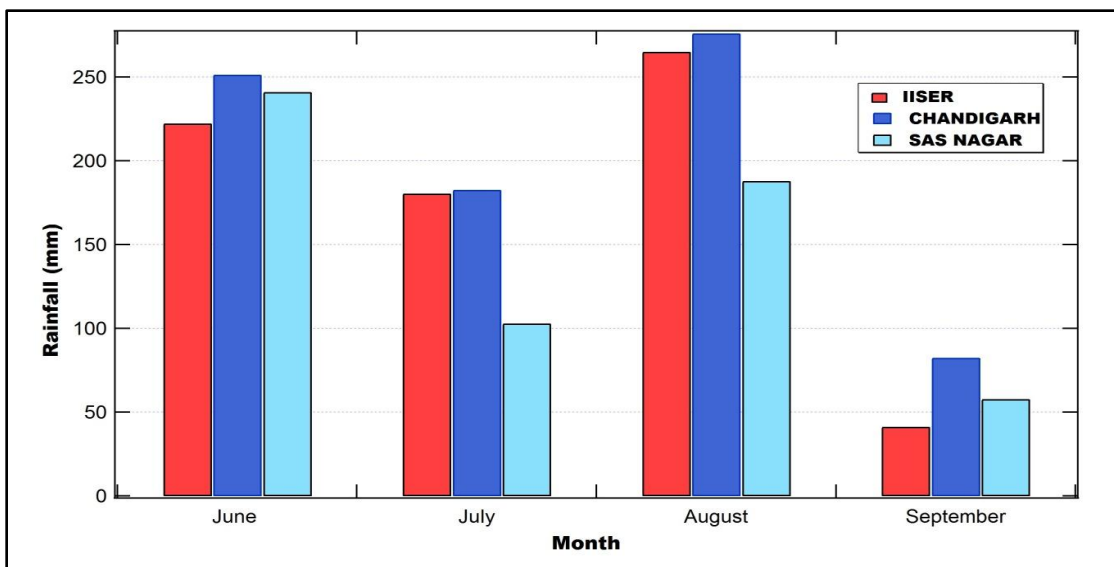
populated and polluted Indo-Gangetic Plain points to the fact that wet scavenging efficiency due to monsoon rains strongly cleanses the troposphere.

The amount of rainfall received at the measurement site was measured using a tipping bucket rain gauge sensor (MODEL 370C/372C, Met One Instruments, US) for the monsoon season of 2013 starting from 6-06-13 to 12-09-2013. During this period, the station received rainfall on 44 days. The highest rainfall in a single day was received on 9<sup>th</sup> August (89.7 mm) and the total amount of rainfall received during the season is 709.3 mm. Figure 3.2 shows the time series plot of the one-minute data in Monsoon 2013 for the rainfall events. The purple dot points indicate a rain event and the red dot points and the horizontal lines parallel to the x-axis indicate dry conditions. Figure 3.3 shows the monthly rainfall amount received at the measurement site in comparison to the nearby stations of Chandigarh and SAS Nagar. The rainfall data for Chandigarh and SAS Nagar were obtained from the official website of Indian Meteorological Department (IMD) (<http://www.imd.gov.in/>)<sup>18</sup>. The data acquired from the measurement site shows better agreement with Chandigarh data. The rainfall data of

Chandigarh is based on measurements from a single rain gauge sensor located at the Indian Meteorological Department (IMD) office(sector -32) which is ~10km away from the measurement site while SAS Nagar data shows the arithmetic average of rainfall of all the stations under the district with the nearest one being Kharar (~15 km) .



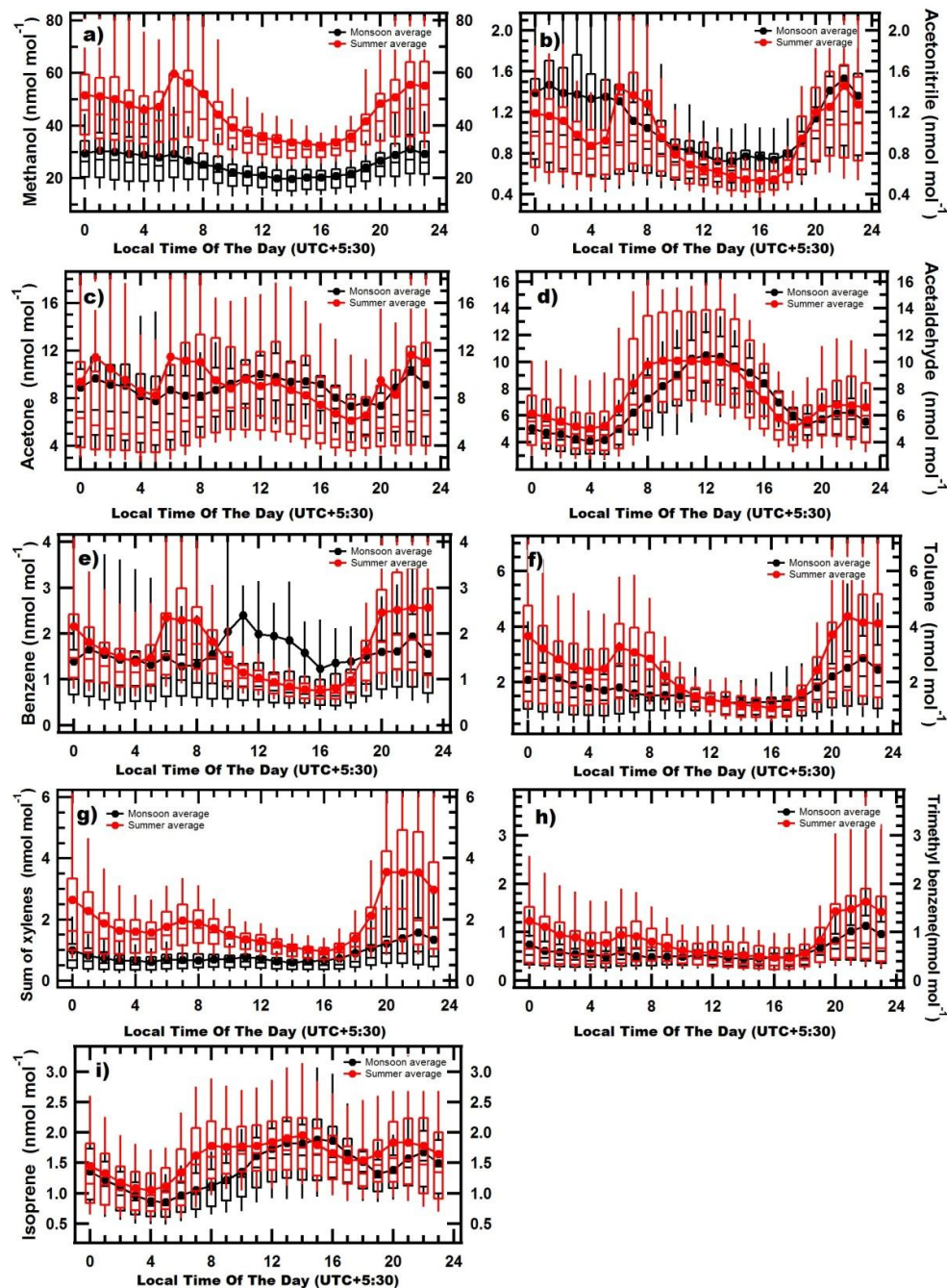
**Figure 3.2:** Time series plot of the one-minute data in Monsoon 2013 for the rainfall events.



**Figure 3.3:** Monthly rainfall received at IISER Mohali, SAS Nagar and Chandigarh during monsoon 2013.

## 3.2 Diel variability of volatile organic compounds during summer and monsoon season in 2013

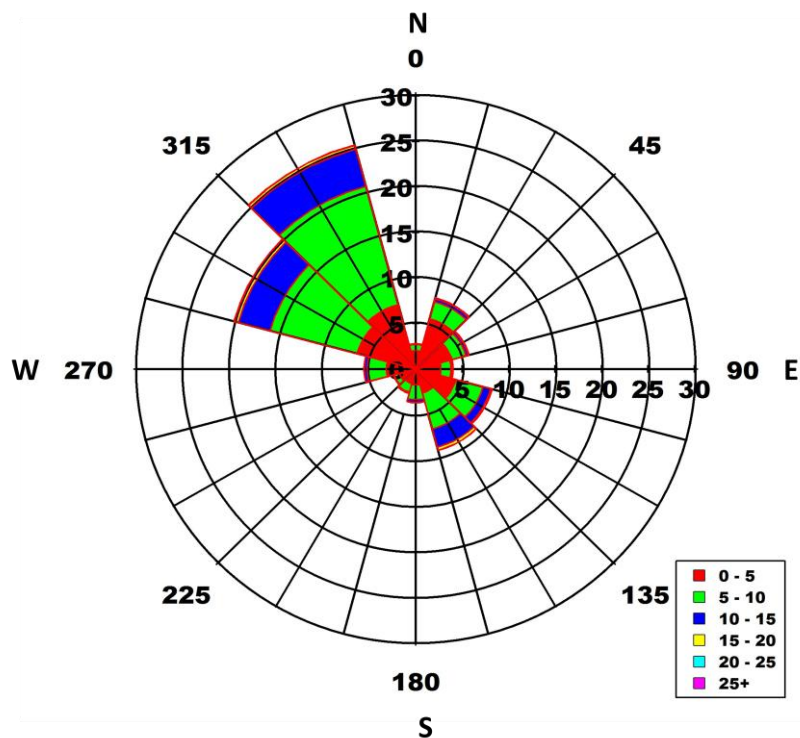
The VOC data for methanol, acetonitrile, acetone, acetaldehyde, benzene, toluene, Sum of xylenes, sum of trimethyl benzene isomers and isoprene reported in this work is the first ambient data set reported from the measurement site for the entire season of summer (2/28/2013-6/6/2013) and monsoon (6/6/2013-21/9/2013). In order to evaluate how the levels of the measured species during monsoon compare with summertime measurements diel box and whisker plots for all the aforementioned VOCs were made. The red markers in figure 3.4 shows the diel box and whisker plot of (a) methanol, (b) acetonitrile, (c) acetone (d) acetaldehyde, (e) isoprene, (f) benzene, (g) benzene and (h) toluene, (g) sum of C8-aromatics (xylene isomers and ethyl benzene), (h) sum of C9-aromatics (isomers of Trimethyl benzenes, (i) isoprene, derived from all measurements ( $n > 140,000$  for each species) during summer 2013 starting from 2/28/2013 to 5/6/2013 at the measurement site. The width of the box represents the interquartile range (25th and 75th percentiles), while the whiskers represent the 10th and 90th percentiles of the data. In each plot, the median is shown as a cross, while the average is shown as a solid black circle. The time on the horizontal axis represents the start time of the corresponding hourly bin. The hourly average values during summer 2013 ranged between  $32 \text{ nmol mol}^{-1}$  to  $60 \text{ nmol mol}^{-1}$  for methanol,  $0.5 \text{ nmol mol}^{-1}$  to  $1.5$  for acetonitrile,  $6 \text{ nmol mol}^{-1}$  to  $12 \text{ nmol mol}^{-1}$  for acetone,  $5 \text{ nmol mol}^{-1}$  to  $10.5 \text{ nmol mol}^{-1}$  for acetaldehyde,  $0.7 \text{ nmol mol}^{-1}$  to  $2.6 \text{ nmol mol}^{-1}$  for benzene,  $1 \text{ nmol mol}^{-1}$  to  $4.4 \text{ nmol mol}^{-1}$  for toluene,  $0.9 \text{ nmol mol}^{-1}$  to  $3.6 \text{ nmol mol}^{-1}$  for C8-aromatics (sum of xylenes),  $0.4 \text{ nmol mol}^{-1}$  to  $1.7 \text{ nmol mol}^{-1}$  for C9- aromatics (sum of trimethyl benzene isomers) and  $1 \text{ nmol mol}^{-1}$  to  $2 \text{ nmol mol}^{-1}$  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 ( $1.9 \text{ nmol mol}^{-1}$ , 13: 00-14:00). Another interesting observation was the decrease in mixing ratio of VOCs methanol by a factor of 2 between 06:00 and 11:00 LT due to the dilution effect of the daytime boundary layer growth for benzene ( $2.4 \text{ nmol mol}^{-1}$  to  $1.2 \text{ nmol mol}^{-1}$ ) and toluene ( $3.3 \text{ nmol mol}^{-1}$  to  $1.5 \text{ nmol mol}^{-1}$ ). The mixing ratio of methanol was decreased by a factor of 1.6 during the same period ( $59.7 \text{ nmol mol}^{-1}$  to  $37 \text{ nmol mol}^{-1}$ ). The wind rose



**Figure 3.4:** Diel box and whisker plot of (a) methanol, (b) acetonitrile, (c) acetone, (d) acetaldehyde, (e) benzene and (f) toluene, (g) sum of C8-aromatics (xylene isomers and ethyl benzene), (h) sum of C9-aromatics (isomers of Trimethyl benzenes), (i) isoprene, derived from all measurements during monsoon 2013 (black markers,  $n > 150,000$  for each species) and summer 2013 (red marker,  $n > 140,000$  for each species) at the measurement site. s) at the measurement site.



analysis was used to determine the prevailing conditions during the measurement and to identify the probable sources. Figure 3.5 shows the rose plot derived from in situ one minute wind direction and wind speed data at the measurement site (30.6670 N, 76.7290 E, 310ma.s.l.) during summer 2013. During summer 2013, the wind prevailing direction was from North West most of the time (>50 %). The land use in the wind sector spanning South to North-West (180–315<sup>0</sup>) is mainly rural and agricultural land.



**Figure 3.5:** Wind rose plot derived from in situ one minute wind direction and wind speed data at the measurement site (30.667<sup>0</sup> N, 76.729<sup>0</sup>E, 310ma.s.l.) during summer 2013.

The black markers in figure 3.4 shows the Diel box and whisker plot of (a) methanol, (b) acetonitrile, (c) acetone (d) acetaldehyde, (e) isoprene, (f) benzene , (e) benzene and (f) toluene, (g) sum of C8-aromatics (xylene isomers and ethyl benzene) , (h) sum of C9-aromatics (isomers of Trimethyl benzenes), (i) isoprene, derived from all measurements (n > 150,000 for each species) during monsoon 2013 at the measurement site. The hourly average values during monsoon 2013 ranged between 18 nmol mol<sup>-1</sup> to 31 nmol mol<sup>-1</sup> for methanol, 0.7 nmol mol<sup>-1</sup> to 1.6 for acetonitrile, 7 nmol mol<sup>-1</sup> to 11 nmol mol<sup>-1</sup> for acetone,

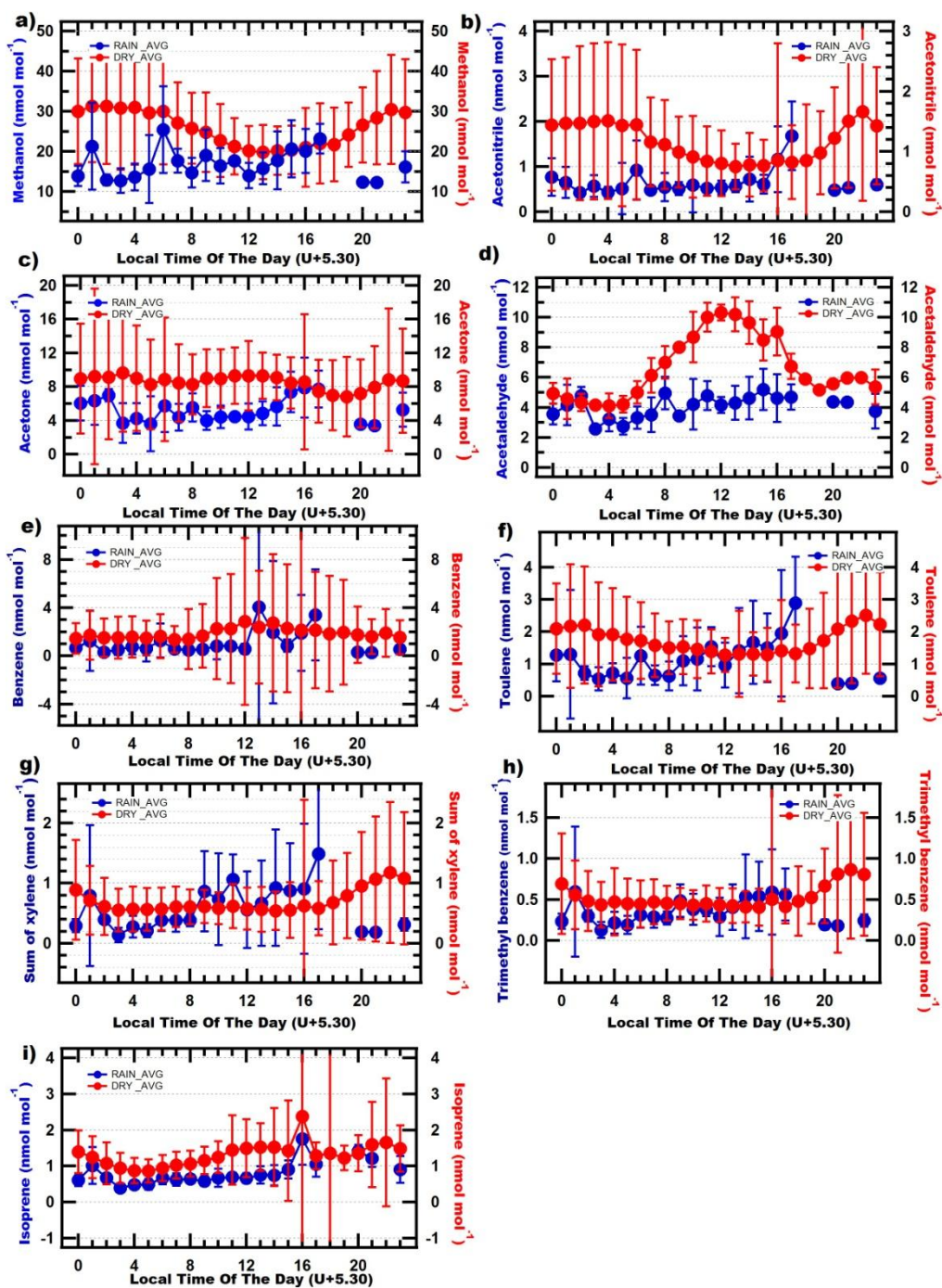
5 nmol mol<sup>-1</sup> to 10.5 nmol mol<sup>-1</sup> for acetaldehyde, 1.2 nmol mol<sup>-1</sup> to 2.4 nmol mol<sup>-1</sup> for benzene, 1.2 nmol mol<sup>-1</sup> to 2.9 nmol mol<sup>-1</sup> for toluene, 0.5 nmol mol<sup>-1</sup> to 1.8 nmol mol<sup>-1</sup> for C8-aromatics (sum of xylenes), 0.4 nmol mol<sup>-1</sup> to 1.2 nmol mol<sup>-1</sup> for C9- aromatics (sum of trimethyl benzene isomers) and 0.8 nmol mol<sup>-1</sup> to 1.9 nmol mol<sup>-1</sup> for isoprene. A diurnal cycle in mixing ratios with daytime maxima similar to that of summer 2013 was observed for both isoprene and acetaldehyde in monsoon 2013 . The isoprene levels peaked between 14:00-15:00 (1.82 nmol mol<sup>-1</sup> ) and acetaldehyde levels peaked between 12:00 - 13:00 (10.5 nmol mol<sup>-1</sup> ) during the day.

In general, there are several factors that could affect the concentrations of VOCs in the summer and the monsoon. Chemical removal of VOCs, especially by OH radicals, is faster during the summer than monsoon as more solar radiation and higher temperatures enhance the photochemical production of OH radical, increasing the chemical removal reaction rate. To factor out the effect of solar radiation on the ambient concentration of VOCs nighttime (18:00 - 00:00) values during summer and monsoon season were compared. It was observed that even with proper dilution due to an increased mixed layer height during summer average nighttime mixing ratios for VOCs for summer are notably higher than the average nighttime mixing ratios during monsoon. This indicates the significance of wet removal of VOCs as more number of rainy days in monsoon season would cause the washout of trace gases. Thus, accumulation of VOCs is reduced in the ambient atmosphere during the monsoon season when compared to summer leading to lower mixing ratios.

### **3.3 Diel variability of volatile organic compounds at the measurement site during rain events and dry conditions**

Figure 3.6 shows the diel variability plots for the volatile organic compounds methanol, acetone, acetonitrile, isoprene, acetaldehyde, toluene, benzene, sum of xylenes and sum of trimethyl benzene derived from all measurements filtered for South East wind direction





**Figure 3.6:** shows the average diel variability plot of (a) methanol, (b) acetonitrile, (c) acetone, (d)acetaldehyde, (e) benzene and (f) toluene (g) sum of xylene (h) sum of trimethyl benzenes (i) isoprene derived from all measurements during rain events and dry conditions of monsoon 2013 filtered for South East ( $90^{\circ}$  -  $180^{\circ}$ ) direction at the measurement site.

sector ( $90^{\circ}$  -  $180^{\circ}$ ) during monsoon 2013 at the site. Blue and red markers correspond to hourly average values of ambient concentrations observed during rain events and dry conditions respectively. As we can see in most cases, during rain events the ambient concentrations of VOCs are lower compared to the concentrations during dry conditions. The compounds with lower molecular weight and higher solubility like methanol, acetonitrile, acetaldehyde, and acetone also have lower concentrations during rain events compared to dry conditions. In the case of aromatic VOCs and isoprene the difference in concentration between dry conditions and rain events are low when compared to that of oxygenated VOCs as they are less soluble.

### **3.4 Disentangling factors responsible for difference in concentration of VOCs between rain events and dry conditions**

There are other processes in addition to wet scavenging due to which the ambient concentration of volatile organic compounds can be higher or lower during the rain event relative to the dry periods. We have studied the influence of such factors on ambient concentrations of VOCs and quantified their contribution to the observed differences. The factors and their roles are explained in section 3.4. 1and were considered while calculating the wet scavenging efficiency.

#### **3.4.1 Fetch Region /Emissions**

The region over which the wind blows prior to arrival at the site constitutes the fetch region and will affect the concentration of trace gases in the atmosphere due presence of specific sources in it. If the wind is blowing from an urban area VOC levels are likely to be different from the case in which the air is blowing from another direction, for example a rural land due to heterogeneity of emission sources . Figure 3.7a and 3.7b shows the rose plot derived from in situ one minute wind direction and wind speed data at the measurement site ( $30.6670^{\circ}$  N,  $76.7290^{\circ}$  E, 310ma.s.l.) during dry conditions and rain events of monsoon 2013 respectively.

To ensure that the difference in concentration of VOCs during dry conditions and rain events are not influenced by the fetch region the air masses were filtered for wind sector spanning between 90<sup>0</sup> -180<sup>0</sup> (outlined in Figure 4b) as this is the most frequent wind sector during both rain event and dry conditions. This procedure ensures that heterogeneity of emission sources due to different fetch regions in the analyzed dataset will not contribute to observed concentration differences.

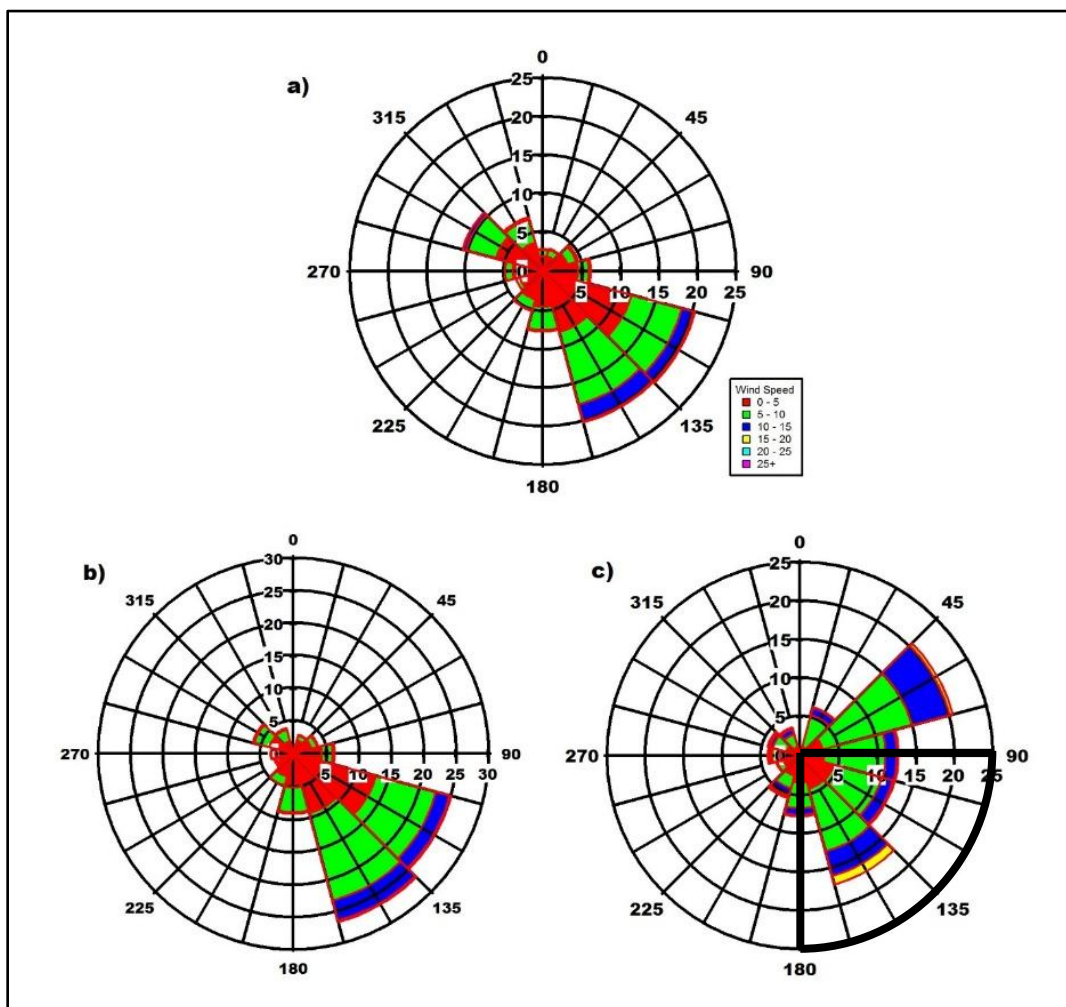
### 3.4.2 Mixed layer height

The ambient concentrations of VOCs are strongly affected by the mixing layer height since it determines the volume of air into which the gases are emitted. The mixed layer height varies significantly with the time of a day and meteorological conditions. Figure 3.8 shows the diel variability profile of mixed layer at the measurement sites during dry conditions and rain events of monsoon 2013. The hourly mixed layer height for the measurement site (30.667°N, 76.729°E, 310m a.s.l.) was computed using NOAA HYSPLIT\_4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) model's Global Data Acquisition System (GDAS) meteorology as input (Draxler and Rolph., 2013)<sup>19</sup>. Due to the fact that the model does not always resolve the terrain gradient accurately for simulations near the Himalayan foothills, we applied an additional filter and only trajectories consistent with the measurement site, Mohali, being located in the plain (< 400ma.m.s.l.) and Shimla, a mountain site at 31.103\_ N, 77.172\_ E, being located in the mountains (> 400ma.m.s.l.), were considered. As expected, the mixed layer height evolves diurnally. Under dry conditions, when it is sunny the mixed layer has the maximum height (2560.2 m, 14:00-14:59). This occurs as a result of the strong heating of the ground by the solar radiation and turbulence. During rain events, when it is cloudy the solar radiation is weak and the mixing layer height is lower (1581.5, 14:00-14:59) due to the change in surface heat flux. To constrain the influence of mixed layer height dynamics on the difference in concentration of VOCs between rain events and dry conditions a correction equation has been used.

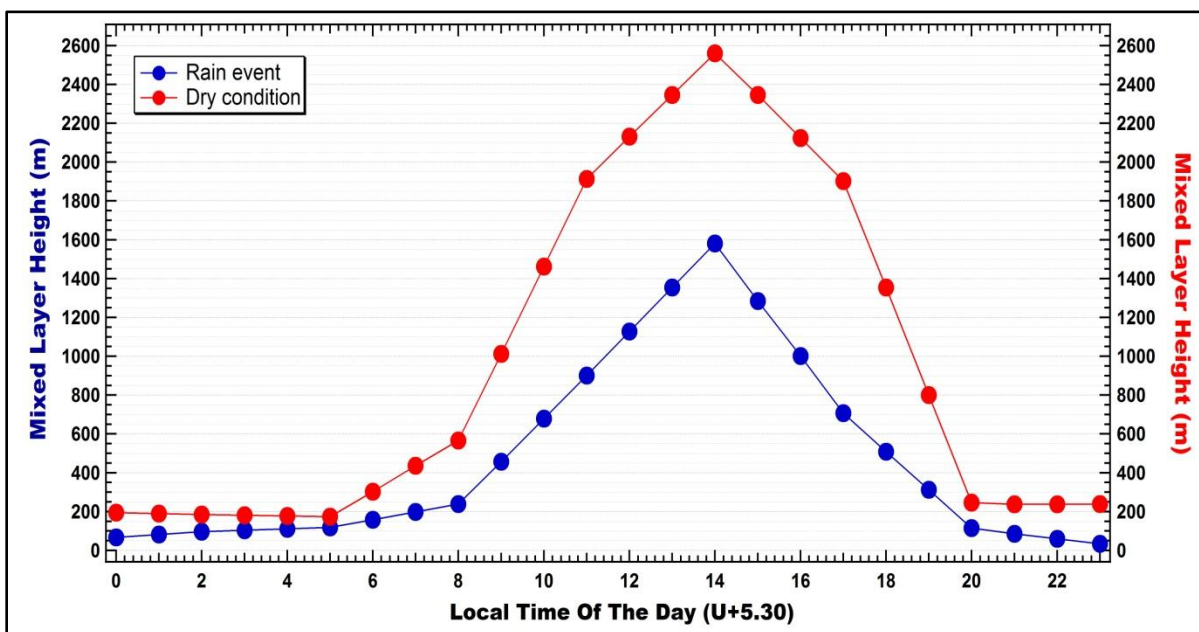
$$\text{Corrected Dry (x)} = C_x \times (\text{ML Dry} / \text{ML Rain}) \text{----- (1)}$$

C<sub>x</sub> - Mixing ratio of x in ppb; ML - Mixed Layer Height

The hourly average mixing ratio of VOCs during dry conditions is multiplied by the ratio between mixed layer height during dry conditions and mixed layer height during rain event for that particular hour. Figure 3.9 shows average diel profile of VOCs for dry conditions and rain events along with the corrected profile for the complete monsoon season of 2013 filtered for South East ( $90^{\circ}$  - $180^{\circ}$ ) direction. The scavenging ratios were further calculated using the corrected dry conditions values.



**Figure 3.7:** Wind rose plot derived from in situ one minute wind direction and wind speed data at the measurement site (30.6670 N, 76.7290 E, 310m a.s.l.) during monsoon 2013 (a) , dry conditions (b) and rain events (c) of monsoon 2013 respectively. The outlined region indicates the South-East wind sector ( $90^{\circ}$ - $180^{\circ}$ ).



**Figure 3.8:** average diel profile for mixed layer height for the entire season of monsoon 2013 (108 days) at the measurement site.

### 3.4.3 Solar radiation

Biogenic VOCs such as isoprene and oxygenated VOCs such as methanol, acetaldehyde, and acetone can be directly emitted into the atmosphere from various natural (Fall and Benson, 1996)<sup>20</sup> and anthropogenic sources. The oxygenated VOCs are also formed as a result of the gas phase photooxidation of precursor organic compounds in the atmosphere. The largest source of acetaldehyde is thought to be the photochemical oxidation of isoprene and other VOCs such as alkanes containing more than 1 carbon atoms and alkenes containing more than 2 carbon atoms (Atkinson et.al, 2006b)<sup>21</sup>. Also solar radiation induced photolysis and photochemical oxidation by OH radical are the major removal mechanism for the VOCs<sup>22</sup>. Therefore, any increase or decrease in the intensity of the solar radiation can lead to changed abundance of such VOCs in the atmosphere. Figure 3.10 shows the diel variability plot of solar radiation derived from all in situ one minute measurements during rain events and dry conditions of monsoon 2013 at the measurement site (n > 10, 0000). It can be seen that during daytime the maximum solar radiation intensity decreases by a factor of

approximately ten times during rain events as compared to that of dry conditions. No significant difference was observed during early morning (00:00 - 06:00) and nighttime values (18:00 - 00:00) of solar radiation intensity between rain events and dry conditions. Therefore to constrain the effect of solar radiation and to derive concentration differences of VOCs during rain events and dry conditions solely due to the wet removal process, scavenging ratios calculated for nighttime hours were considered for further analysis.

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

The scavenging of volatile organic compounds by monsoon rain was studied using scavenging ratios, which is a simplified approach for examining the overall wet deposition process based only on the concentration of a gaseous compound during rain events and dry conditions. Scavenging ratios were determined as follows:

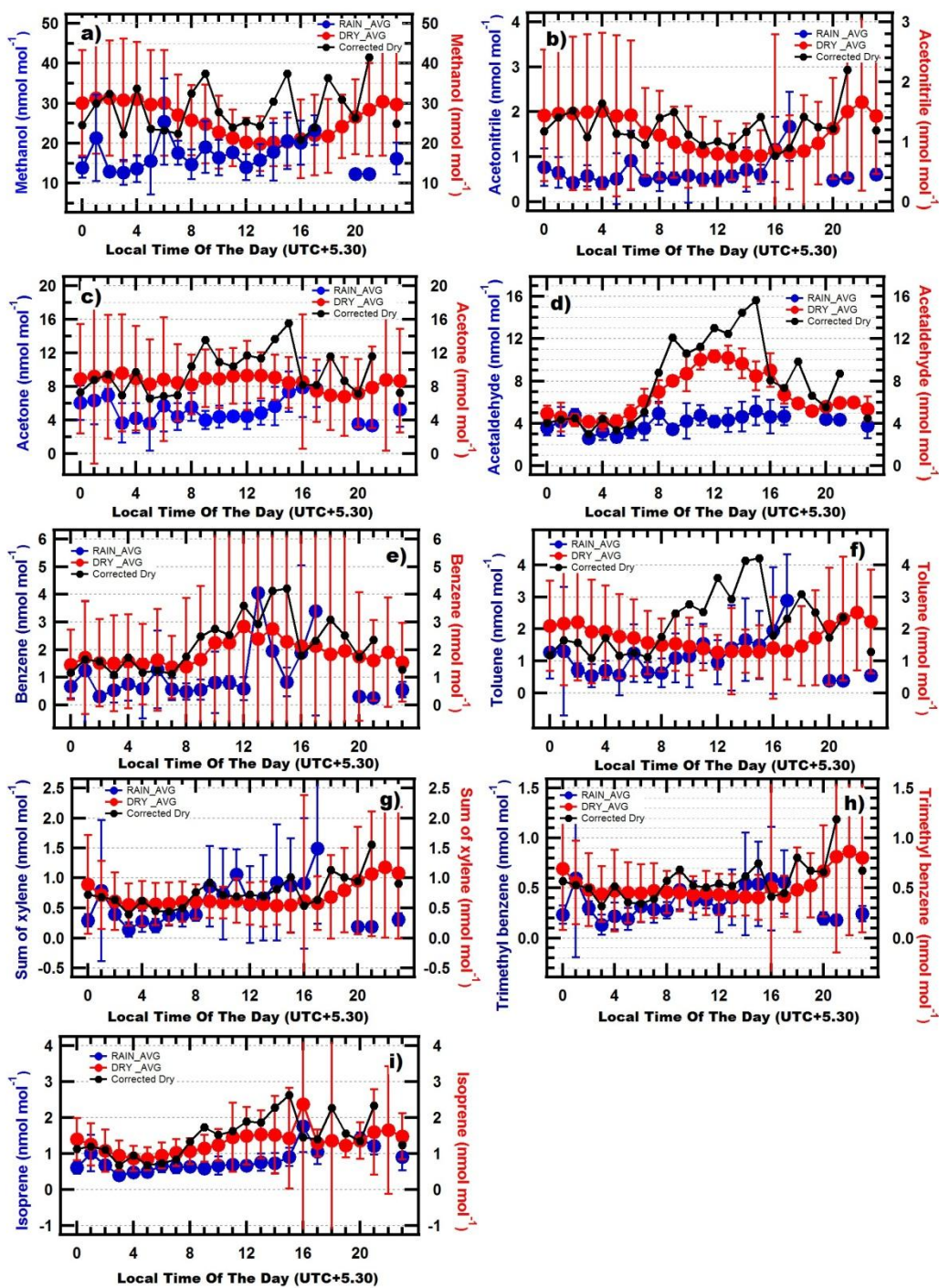
$$\text{Scavenging ratio (x)} = \text{Corrected Dry (Cx)} / \text{Rain (Cx)} \text{ -----(2)}$$

Cx - Mixing ratio of x in ppb; ML - Mixed Layer Height

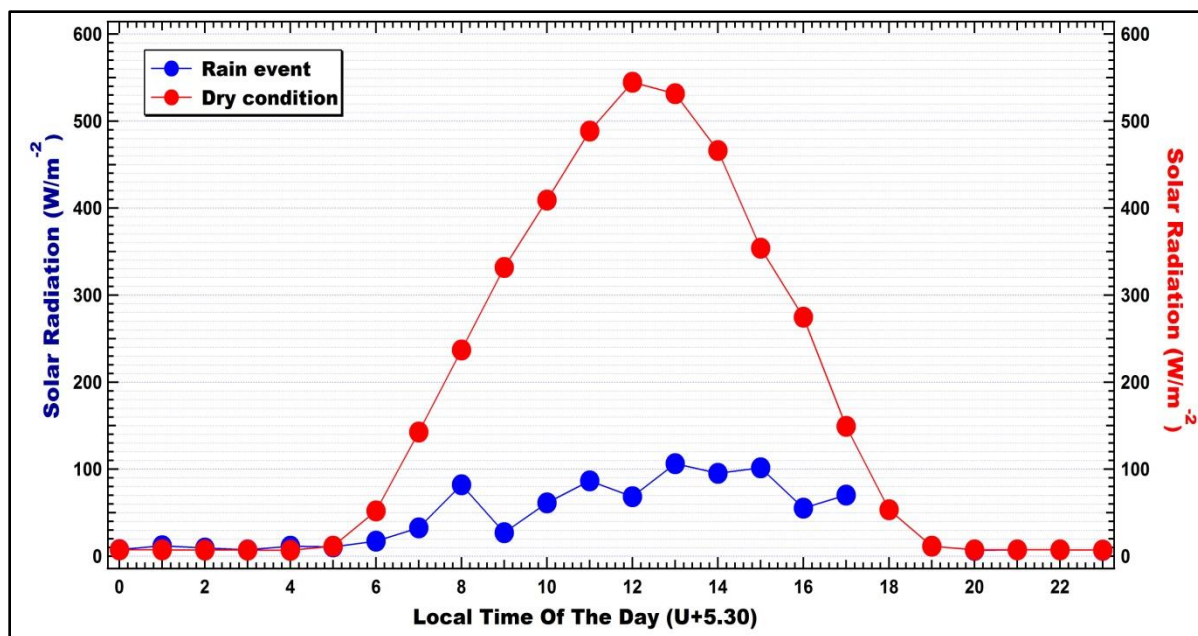
### **3.6 Wet scavenging efficiency of VOCs in relation to their solubility**

The wet scavenging ratios were determined for the following reactive volatile organic compounds: methanol, acetone, acetonitrile, isoprene, acetaldehyde, toluene, benzene, sum of xylenes and sum of trimethyl benzene using the mixed layer corrected dry values. Three different time periods of a day were selected (early morning, 00:00-05:00 ; daytime, 06:00-17:00) ; nighttime, 18:00-23:00) and the calculated scavenging ratios were plotted against the Henry's law constant (Sander R., 1999)<sup>23</sup> for all the VOCs.





**Figure 3.9:** Average diel variability profile of (a) methanol, (b) acetonitrile, (c) acetone, (d)acetaldehyde, (e) benzene and (f) toluene (g) sum of xylene (h) Sum of trimethyl benzene (i) isoprene for dry conditions , rain events along with the mixed layer corrected profile for the complete monsoon season of 2013 filtered for South East ( $90^0 - 180^0$ ) direction.

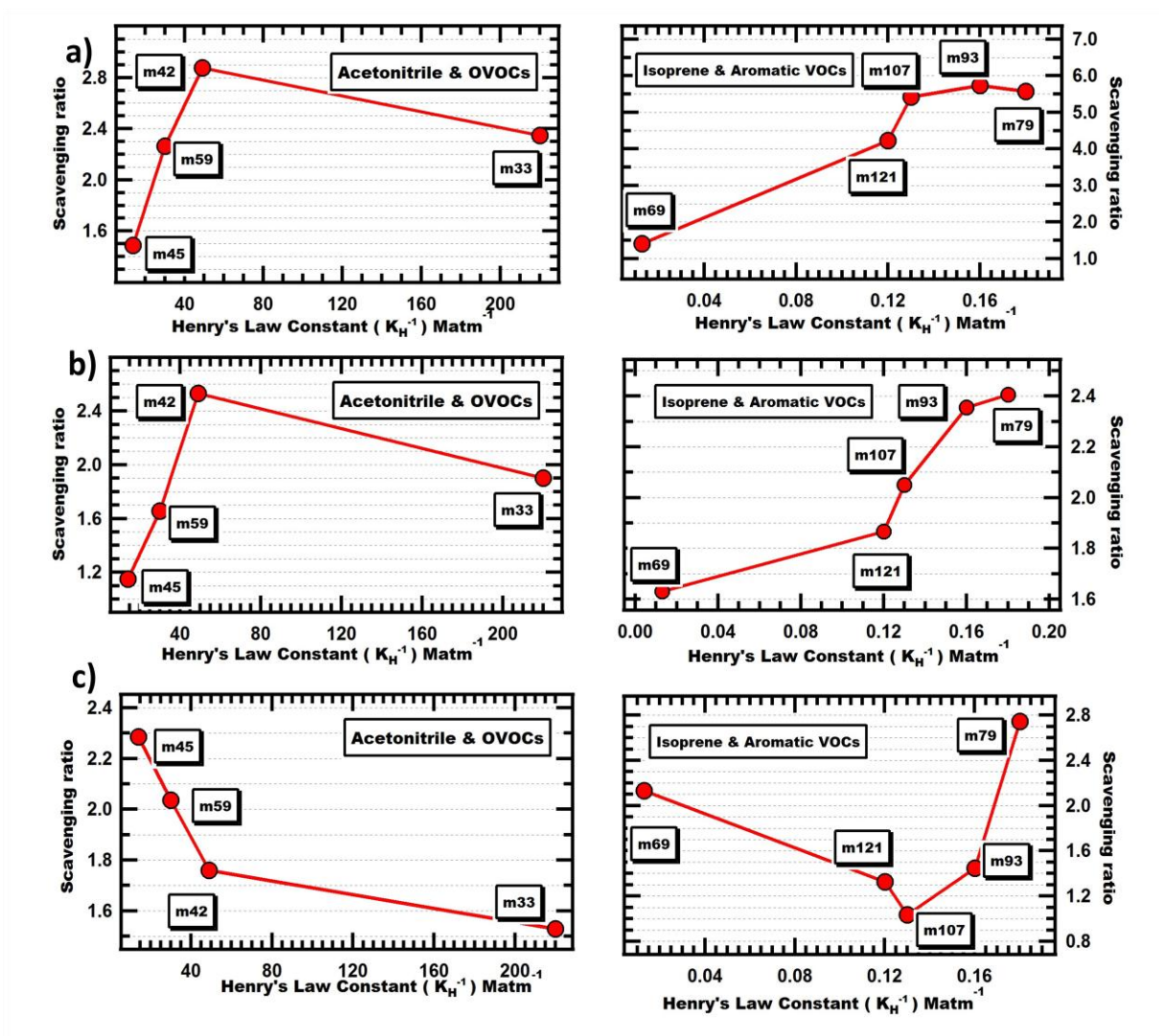


**Figure 3.10:** The diel variability profile of solar radiation derived from all in situ one minute measurements during rain events and dry conditions of monsoon 2013 at the measurement site ( $n > 10,000$ ).

During the night time (Figure 3.11a) and early hours of the day (Figure 3.11b) the scavenging ratios of all VOCs (except methanol) predominantly follow the solubility trend. The observed trend in wet scavenging efficiency for VOCS were : acetonitrile (2.87) > methanol (2.35) > acetone (2.26) > acetaldehyde (1.49) for oxygenated VOCS and benzene (5.75) > toluene sum of xylenes (5.42) > trimethyl benzene (4.22) > isoprene (1.41) for aromatic VOCs and olefins. Despite the high solubility of methanol, the scavenging ratio of methanol was not the highest. The likely explanation for the anomalous behaviour of methanol is that even in the absence of rain events, the presence of humid conditions contribute significantly to the removal of highly soluble methanol thus minimizing rain event's contribution. Another notable observation is the more efficient scavenging shown by VOCs during night and early morning hours compared to daytime hours. During daytime(06:00 -17:00) photochemistry, anthropogenic activities and the complex dynamics of planetary mixed layer perturbs the wet scavenging efficiency of rain water and complicate matters. Figure 3.11c shows the scavenging ratio vs. Henry's law constant graph plotted for aromatic and oxygenated VOCs during daytime. Interestingly we don't see any dependence



of the VOCs on solubility. Most probable reason could be that there are more one mechanisms acting at the same time.



**Figure 3.11:** Plot of wet scavenging efficiency of monsoon rain against the Henry's law constant for methanol(m33), acetonitrile(m42), acetone (m59) and acetaldehyde (m45), for benzene (m79), toluene (m93), sum of xylene (m107), Sum of trimethyl benzene (m121) and isoprene (m69) during (a) nighttime (18:00 – 23:00), (b) morning (00:00 – 05:00) and (c) daytime (05:00 – 17:00).

# Chapter 4

## Summary and Conclusions

The purpose of the study was to examine diel and seasonal (between summer and monsoon) variability and assess the importance of wet scavenging in controlling ambient concentrations of reactive VOCs. 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 concentrations during period June- September 2013 in Mohali (30.667N; 76.729E). The average mixing ratios of methanol, acetone, isoprene, acetaldehyde, toluene, benzene, sum of xylenes and sum of trimethyl benzenes isoprene observed at the site in the northwest Indo-Gangetic Plain in monsoon 2013 were generally lower compared to those observed for summer 2013 at the same site. The lower concentrations of VOCs in monsoon season in spite of the fact that the fetch region is the more densely populated and polluted Indo-Gangetic Plain indicates that atmospheric removal mechanism play a more dominant role than emission sources during the monsoon season.

Factors which impact the ambient concentration during rain events and dry periods such as boundary layer dilution effect, photochemistry and change in fetch region for the VOC emission sources were systematically ascertained to derive the concentration differences purely attributable to wet scavenging. The scavenging ratios thus calculated was plotted against Henry's law constant (which characterizes the solubility of a gas) for all the VOCs. The major observation was that the photochemically produced VOCs don't follow the solubility trend during the daytime. Photochemistry, anthropogenic activities and the

complex dynamics of planetary mixed layer strongly affect wet scavenging and due to poorly understood mechanistic aspects, their synergistic effect are not be captured by current atmospheric models, which rely instead on the solubility of compounds as proxies for considering the wet scavenging efficiency<sup>24</sup> . Discrepancies were found for methanol between the wet scavenging efficiency predicted using its solubility and the value observed from ambient field data. This shows that wet scavenging ratios derived from ambient field measurements provide a more accurate method to account for wet removal of VOCs.

This study is the first attempt worldwide to determine the wet scavenging efficiency for the reactive VOCs such as methanol, acetone, acetaldehyde, isoprene, benzene, toluene and xylenes using a high temporal resolution (every minute) ambient field dataset. Further studies at other urban sites (the present study is characteristic of a suburban site) or forested sites and at different latitudes would highlight the differences in wet scavenging ratios for varied chemical environments. Employing only the solubility values of compounds for wet scavenging efficiencies is clearly an inadequate representation for the wet removal of the most abundant VOCs such as methanol.

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