Quantification of isoprene emission fluxes using a dynamic branch cuvette system from poplar (*Populus deltoides*) growing in North India

Priya Yadav
(MS14169)

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Certificate of Examination

This is to certify that the dissertation titled **"Quantification of isoprene emission fluxes using a dynamic branch cuvette system from poplar (*Populus deltoides*) growing in North India"** submitted by **Ms. Priya Yadav** (Reg. No. MS14169) 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	Dr. B. Sinha	Dr. A. Ambili
(Supervisor)		

Dated:

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. V. 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.

Priya Yadav

(Candidate)

Dated:

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. V. Sinha
(Supervisor)

Acknowledgement

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Notation (Abbreviations)

1. VOC	Volatile Organic Compound
2. BVOC	Biogenic Volatile Organic Compounds
3. PAR	Photosynthetically Active Radiation
4. TD-GC-FID	Thermal Desorption Gas Chromatography Flame Ionization Detector
5. PTR-QMS	Proton Transfer Reaction Quadrupole Mass Spectrometry
6. CRDS	Cavity Ring Down Spectrometry
7. IGP	Indo-Gangetic Plain

Contents

Abstract

Isoprene is the single largest contributor to the overall biogenic volatile organic compound (BVOC) emissions and can form secondary pollutants such as tropospheric ozone on reacting with anthropogenically emitted nitrogen oxides affecting the air quality and climate. *Populus deltoides* is an important commercial timber source and planted over an area of ~3120 km^2 as part of agroforestry practices in north India alone. Here, we present measurement results quantifying isoprene emission fluxes (EF_{iso}) from *Populus deltoides* growing in their natural environment in north India during the monsoon and post-monsoon seasons using dynamic branch cuvettes coupled to real-time Proton Transfer Reaction- Mass Spectrometry (PTR-MS) and Thermal Desorption Gas Chromatography-Flame Ionization Detection (TD-GC-FID). There was excellent agreement between isoprene measurements obtained using the PTR-QMS and TD-GC-FID (r=0.98). We also measured water vapor and carbon dioxide using a Cavity Ring Down Spectrometer (CRDS) along with PAR and temperature for mechanistic insights regarding the emission process. The daytime measured isoprene emission flux (EF_{iso}) ranged from 0.1-67.8 µg g^{-1} hr^{-1} and 0.2-18 µg g^{-1} hr^{-1} for the monsoon and post-monsoon seasons, respectively. Previous studies using other methods, have reported average (normalized to 1000 µmol m^{-2} s^{-1} and 30 °C) isoprene emissions ranging from 37 µg g^{-1} hr^{-1} by *Evans et al. (1982)* to 53.6 ± 11 µg g^{-1} hr^{-1} by *Singh et al.* We will discuss the relevance of our results in the context of EF_{iso} calculated using the MEGAN BVOC emission model and regional air quality.

Chapter 1

Introduction:

1.1 What are BVOCs

Biogenic volatile organic compounds (BVOCs) are the VOCs which are emitted by living beings such as plants, shrubs, humans, etc. BVOCs play an important role in atmospheric chemistry and carbon cycle. Terrestrial plants are the major contributor of the BVOCs in the atmosphere. Isoprenoids represent a class of heterogeneous compounds consisting of a wide range of reactive volatile compounds (isoprene, monoterpenes, and sesquiterpenes) which are emitted by most plant species. Among them, isoprene is the isoprenoid which is emitted in the enormous quantity by most of the plant species (Guenther et al., 1999; Kesselmeier and Staudt, 1999) (*Malik et al., 2018*).

1.2 Sources and sinks of isoprene

Terrestrial plants are the main source of isoprene. The estimated annual global emission of isoprene is about 400-600 TgC yr^{-1}, obtained from the studies conducted by (Guenther et al., 1995; Arneth et al., 2008; Dunn-Johnston et al., 2016; Dani et al., 2017). Table 1.2 a) shows the distribution of isoprene and monoterpenes emission from various sources. The emission of isoprene from plants depends on environmental conditions such as temperature and light. The seasonality of the environmental factors such as temperature, light and water availability also affects the emission of isoprene (Guenther et al., 1991; Guenther et al., 1993; Sharkey and Singsaas, 1995; Penuelas and Llusia, 2001; Guenther et al., 2006; Grote and Niinemets, 2008; Niinemets et al., 2010), (*Malik et al. 2018*). The species isoprene is very reactive, having a life time of 1-2 hours (*Guenther et al. 1995*). The isoprene in atmosphere plays an important role in atmospheric chemistry and results in the formation of photochemical smog and secondary organic aerosols (SOAs) which plays a significant role in cloud formation and precipitation (Andreae and Crutzen, 1997; Poschl et al., 2010; Niinemets et al., 2011; Sun et al., 2012; Waked et al., 2012; Tuankrua et al., 2014). A series of reaction are given below which isoprene underwent as it is emitted in the atmosphere (*Sharkey et al., 2008*):

$RH + OH + O_2 \rightarrow RO_2 + H_2O$

$RO_2 + NO \rightarrow RO + NO_2$

$RO + O_2 \rightarrow R'CHO + HO_2$

$2(NO_2 + O_2 \rightarrow NO + O_3)$

Net: $RH + 4\ O_2 \rightarrow R'CHO + 2\ O_3 + H_2O$

Where RH is a hydrocarbon (a general reaction for all VOCs). Isoprene reacts rapidly with the OH radical present in the atmosphere and forms hydroperoxides (RO_2). In the atmosphere, NO and NO_2 (collectively NO_X) cycle under the influence of sunlight. At night, all NO_X as NO_2 and during day hours sunlight photolysis the NO_2 and leads to one molecule of ozone per NO_2 (Jacob, 1999; Monson and Holland, 2001). And, hydroperoxide reacts with NO to form NO_2 and results in more production of ozone.

Since, BVOC emission rates controls the much of tropospheric OH radical concentration, BVOC emissions may play a major role in determining the growth rate of atmospheric CH_4 and CO concentrations. Since, compounds like CH_4 influence the radiative balance of the atmosphere and thus decides the global temperature and precipitation patterns, there is a clear link between BVOC emissions and Earth climate (*Guenther et al., 1995*).

1.3 Why to study *Populus deltoides*

Populus deltoides is a deciduous and a native to most of the Northern Hemisphere plant species. It is a genus of 25-35 species. India is a native place of four *populus* species and five are the exotic *populus* species which are *Populus ciliata*, *P. gamblei*, *P. Jacquemontii var. glauca*, *P. rotundifolia* and *P. deltoides*, *P. alba*, *P. euphratica*, *P. nigra, P. laurifolia* respectively (*Country report 2012-2015*).

Here, in this study *Populus deltoides*, an exotic plant species which is planted mostly in the North India for the agroforestry purpose and to improve the economic conditions of the farmers has been studied for its isoprene emission in two seasons monsoon and post-monsoon. *Populus deltoides* is intercropped with all grain, pulse and vegetable crops, have a rotation cycle of 6-8 years with a growth rate of 20-25 $m^3ha^{-1}yr^{-1}$ and an out- turn of 5.05 million tonne/yr fresh wood makes it a most preferable *populus* species to study. In world *Populus deltoides* is native only to Canada and US and is an exotic species to countries like Australia, China, India, Nepal, Netherlands, New Zealand, Pakistan, Sweden, United Kingdom. Figure 1.3 a) shows a map of *Populus deltoides* over the globe and Table 1.3 a) shows the area covered by *Populus deltoides* plantation in India (*Populus deltoides Salicaceae Bartr- Agroforestry Database 4.0*).

The emission of isoprene from this particular plant species has been studied in real time with both PTR-QMS and TD-GC-FID and also CO_2 assimilation was studied with CRDS (Cavity Ring Down Spectroscopy) instrument using a dynamic branch cuvette system (*Ninnemets et al. 2011*). This study includes seasonal variation in isoprene emission affected by temperature, light, relative humidity and CO_2 emission during monsoon and post-monsoon seasons. Moreover, the emissions of isoprene from plants contribute significantly to the global carbon budgets and provide an idea for the estimation of carbon stock especially at forest levels (Dar and Sahu, 2018), (*Malik et al., 2018*).

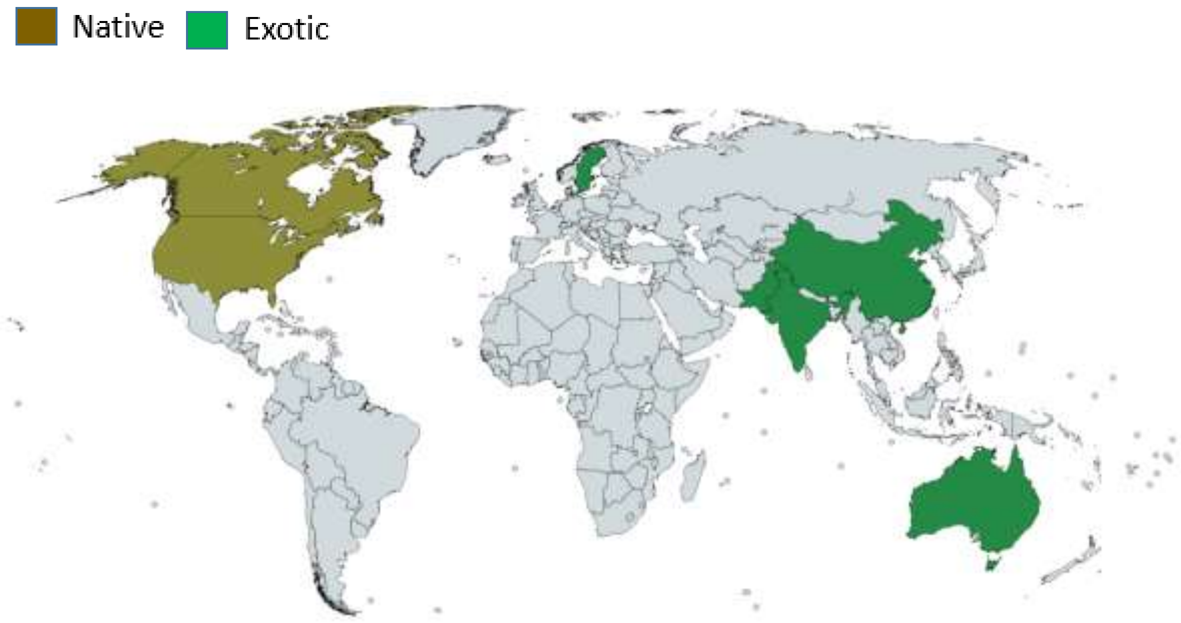
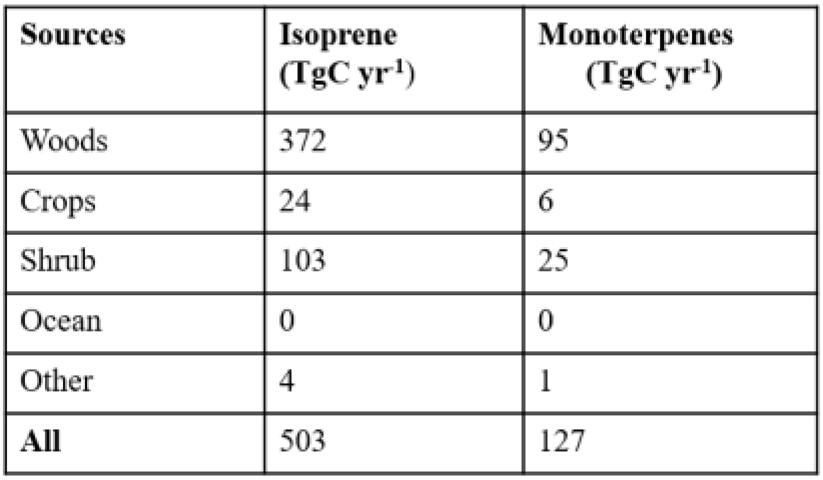


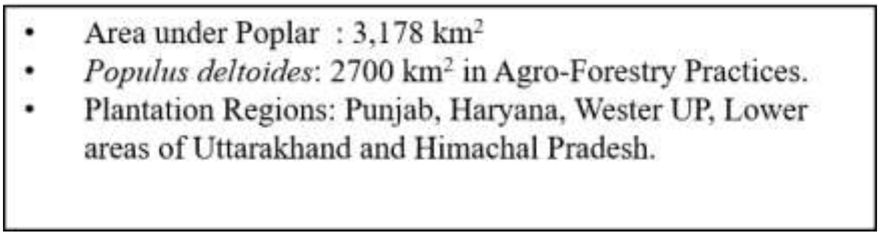
Figure 1.3 a) *Populus deltoides* distribution over the globe **(**https://mapchart.net**)**. Coloring of map is done at mapchart.net site.

Table 1.2.a) World-wide budget of isoprene and monoterpenes emission (*Guenther et al., 1995*).



Sources	**Isoprene (TgC yr^{-1})**	**Monoterpenes (TgC yr^{-1})**
Woods	372	95
Crops	24	6
Shrub	103	25
Ocean	0	0
Other	4	1
All	503	127

Table 1.3 a) Area covered by *Populus deltoides* in India (*Country report 2012-2015*).



- Area under Poplar : 3,178 km^2
- *Populus deltoides*: 2700 km^2 in Agro-Forestry Practices.
- Plantation Regions: Punjab, Haryana, Wester UP, Lower areas of Uttarakhand and Himachal Pradesh.

Chapter 2

Material and methods

2.1 Site description

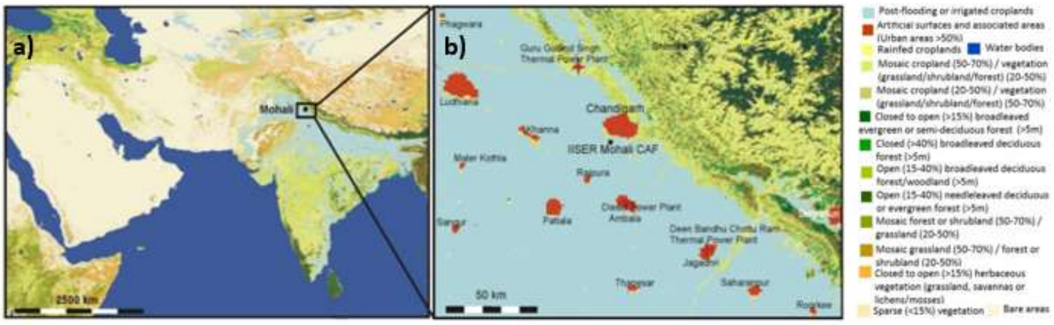


Figure 2.1.: a) Location of the city Mohali in India. **b)** Map of the land classification in a 100 Km × 200 Km surrounding the measurement site (black dot is the location of measurement site, IISER Mohali CAF). Map source – (*Sinha et al., 2014*).

The measurements reported in this work were conducted at the Central Atmospheric Chemistry Facility which is installed in the Central Analytical Facility building in Indian Institute of Science Education and Research Mohali in the city Mohali. Figure 2.1. a) shows the location of the city Mohali a suburban site in the northwest Indo-Gangetic Plain (30.679°N, 76.729°E, 310 m a.s.l), (*Sinha et al., 2014*). The Indo-Gangetic Plain (IGP) is a densely populated area and is the “bread basket” of the South Asia. Figure 2.1. b) shows the land classification and the measurement site is an irrigated cropland thus giving its plant species a different physiological environment than the rest of the India (*Pawar et al., 2017*).

2.2 Experimental details and schematic

2.2.1 Dynamic branch cuvette system

The setup used to measure isoprene emission from *Populus deltoides* was a dynamic branch cuvette system (*Niinemets et al. 2011*). The setup was shown in figure 2.2.1. Ambient air was passed through a filter holder, made of Teflon and sponge material was used to avoid any dust, aerosol particle, etc. to go inside. This filtered ambient air was passed to a KNF pump 1 though a 3/8 inch diameter Teflon tube whose output flow was set to 30 l.p.m. and was sent to a T - piece through a ½ inch, 12 m 2.5 cm long and ¼ inch, 8 cm long Teflon tubes. From the T- piece the filtered ambient air was passed to a series of cartridges as: from T -piece to steel wool water trap cartridge through a ¼ inch, 7.5 cm long Teflon tube to first silica gel water trap trough a ¼ inch Teflon tube of 15 cm length to second silica gel water trap cartridge trough a ¼ inch Teflon tube of 9.2 cm length to charcoal VOC scrubber cartridge through a ¼ inch of Teflon tube of 55cm length. From charcoal VOC scrubber cartridge filtered air was passed to 3-way valve 1 through a ¼ inch Teflon tube of 15 cm length. From here onwards input was sent two Teflon tubes one going the branch cuvette system (the bag used here as a cuvette was Tedlar® bag (polyvinyl fluoride)) having volume $0.071m^3$ and another for the background. From 3-way valve to branch cuvette system a ¼ inch of length 16.2 cm, ½ inch of length 16m 5 cm and ¼ inch, 54 cm Teflon tube was used and for the background a ¼ inch, 17.4 cm long Teflon tube was used. The output (having a well mixture of input filtered air and emission from the branch) from the branch cuvette system to the 3-way valve 2 was passed through a ¼ inch, 54 cm long, ½ inch, 17 m long and ¼ inch, 8 cm long Teflon tubes were used. The second inlet of 3-way valve was attached to the output of the background through a ¼ inch, 8 cm long Teflon tube. And, the third inlet which acted as an output of branch cuvette system and of background was connected with a ½ inch, 67 m 7 cm long Teflon tube to the output KNF pump 2.From the KNF pump 2 the output was passed to the instruments through a 4-way valve to TD-GC-FID, CRDS and PTR-QMS by a ¼ inch, 10 m, ¼ inch, 23 cm and ¼ inch, 37 cm and 1/8 inch, 135 cm long Teflon tubes were used. From this ¼ inch long Teflon tube to GC a T-piece was connected and another ¼ inch, 5 m long Teflon tube was connected to one of the port of CIA Advantage and the left one was for excess flow to go out.

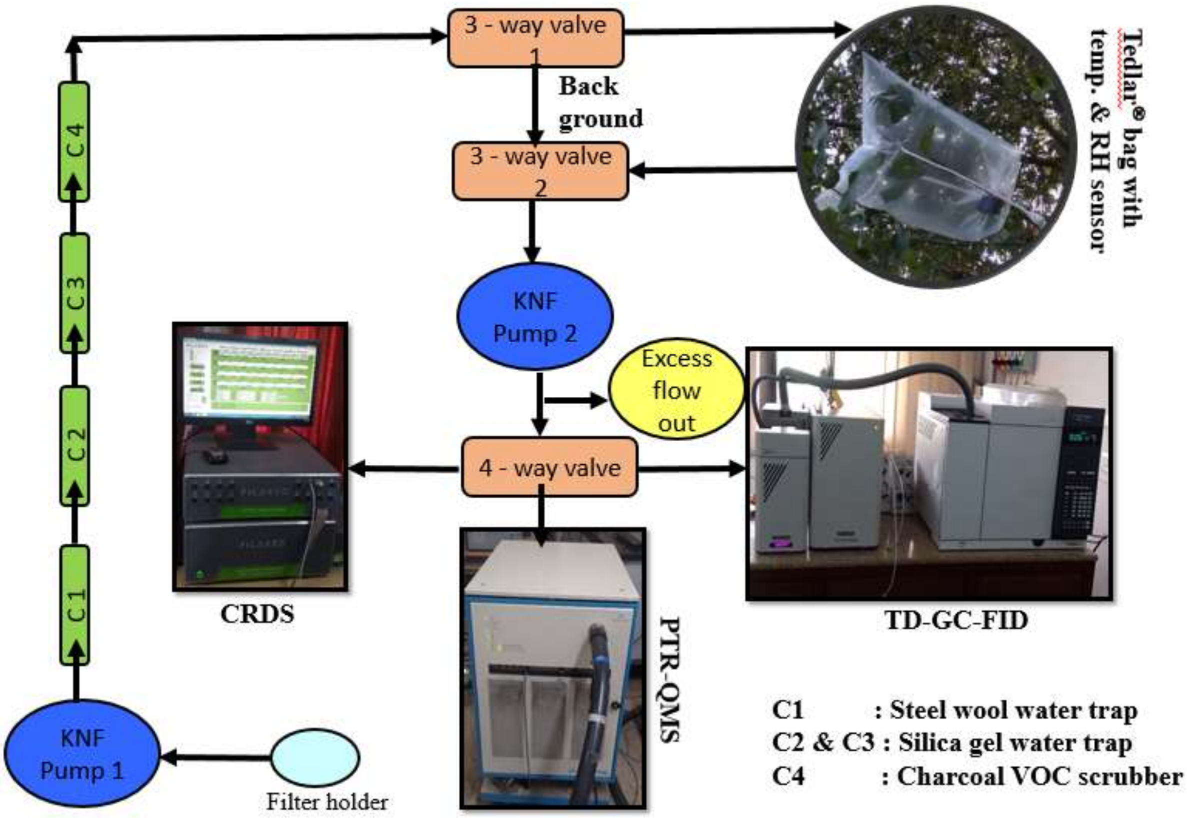


Figure 2.2.1 a) Dynamic branch cuvette system for isoprene measurement.

My project work analyzed the output from the branch cuvette system with TD-GC-FID instrument. And, the analysis with the CRDS and PTR-QMS (Model 11-07HS-088; Ionicon Analytik Gesellschft, Austria, *Sinha et al. 2014*) instrument was done by my other lab members.

The sample from the branch cuvette system was analyzed in two ways – direct injection to the TD-GC-FID and indirectly by collecting the sample into a SilcoCan® Canister and then analyzed with TD-GC-FID. The timings for the sample collection of both the monsoon and post-monsoon seasons for the GC instrument was as:

Table 2.2.1 a) Timings of sample collection.

S.No.	Direct sample injection timings (hour)	Indirect sample collection timings (hour)
1.	20:00	08:00
2.	22:00	10:00
3.	00:00	12:00
4.	02:00	14:00
5.	04:00	16:00
6.	06:00	18:00

The timings were in approximation with an up and down of 15 minutes. Depending upon weather conditions and availability of PAR direct sample injection was done instead of indirect sample collection and this was further decided by the isoprene concentration at that time, checked with PTR-QMS instrument isoprene concentration, which gives on time concentration values. If, concentration of isoprene was < 20 ppbv than direct injection was done otherwise sample was collected in the canister. Prior to the dynamic branch cuvette experiment in both the seasons all the instruments were calibrated with their respective standards. The GC system was calibrated with GC standard and PTR-QMS standard (Apel - Riemer Environmental, Inc., Colorado, USA) containing 13 VOCs at circa 500 ppb with an accuracy > 5 % for both PTR-MS and TD-GC-FID). From the PTR-QMS standard only three compounds are detectable by TD-GC-FID system which were benzene, toluene and isoprene. The GC standard (Chemtron Science Laboratories Pvt. Ltd., Navi Mumbai, India) contains a total 56 compounds which are listed in table 2.2.1 a), having concentration 1 ppm with a ± 5% uncertainty and all are detectable by GC-FID system. Four points were used to calibrate the TD-GC-FID system with GC standard and four points with PTR-QMS standard. These four points were 2 ppbv, 5 ppbv, 10 ppbv and 20 ppbv concentration of standard which was diluted with highly pure zero air from cylinder (Sigma gases, 99.9999%) using a GCU (Gas calibration unit, Ionimed Analytik, Innsbruck, Austria) instrument. The flows of standard and zero air used for dilution at each point are listed in table 2.2.1 b).

CO_2 assimilation data of the branch was obtained from the Cavity Ring Down Spectrometry (CRDS, G2508, Picarro, Santa Clara, USA) with measurement uncertainty $< 4\%$ (*Chandra et al. 2017*).

Photosynthetically active radiation (PAR), soil moisture data were taken from the Decagon device.

Table 2.2.1 b) List of GC standard compounds (*Markes international*, *TDTS 16*).

Molar Mass (g mol^{-1})	**Compound**	**Chemical Formula**	**Molar Mass (g mol^{-1})**	**Compound**	**Chemical Formula**
30.07	Ethane	CH_3CH_3	100.2	2,3-Dimethylpentane	$CH_3CH(CH_3)CH(CH_3)CH_2CH_3$
28.05	Ethene	CH_2CH_2	100.2	3-methylhexane	$CH_3CH_2CH(CH_3)(CH_2)2CH_3$
44.1	Propane	$CH_3CH_2CH_3$	114.22	2,2,4-Trimethylpentane	$CH_3C(CH_3)2CH_2CH(CH_3)CH_3$
42.08	Propene	CH_3CHCH_2	100.21	Heptane	$CH3(CH_2)5CH_3$
58.12	2-Methylpropane	$CH_3CH(CH_3)CH_3$	98.19	Methylcyclohexane	$C_6H_{11}(CH_3)$
58.12	n-Butane	$CH_3(CH_2)2CH_3$	114.22	2,3,4-Trimethylpentane	$CH_3CH(CH_3)CH(CH_3)CH(CH_3)CH_3$
26.04	Acetylene	C_2H_2	92.14	Toluene	$C_6H_5(CH_3)$
56.106	*trans*-But-2-ene	$CH_3CHCHCH_3$	86.18	2-Methylpentane	$CH_3CH(CH_3)(CH_2)2CH_3$

56.106	But-1-ene	$CH_2CHCH_2CH_3$	86.18	3-methylheptane	$CH_3CH_2CH(CH_3)(CH_2)3CH_3$
56.106	*cis*-But-2-ene	$CH_3CHCHCH_3$	114.23	Octane	$CH_3(CH_2)6CH_3$
70.13	Cyclopentane	$(CH_2)5$	106.17	Ethylbenzene	$C_6H_5CH_2CH_3$
72.15	2-Methylbutane	$CH_3CH(CH_3)CH_2CH_3$	106.16	*m*- and *p*-Xylene	$C_6H_4(CH_3)2$
72.15	Pentane	$CH_3(CH_2)3CH_3$	104.15	Styrene	$C_6H_5CHCH_3$
70.13	*trans*-pent-2-ene	$CH_3CHCHCH_2CH_3$	106.16	*o*-Xylene	$C_6H_4(CH_3)2$
70.13	Pent-1-ene	$CH_2CH(CH_2)2CH_3$	128.2	Nonane	$CH_3(CH_2)7CH_3$
70.13	*cis*-Pent-2-ene	$CH_3CHCHCH_2CH_3$	120.19	Isopropylbenzene	$C_6H_5CH(CH_3)2$
86.17	2,2-Dimethylbutane	$CH_3C(CH_3)2CH_3$	120.19	Propylbenzene	$C6H5(CH2)2CH_3$
86.17	2,3-Dimethylbutane	$CH_3(CHCH3)2CH_3$	120.20	*m*-Ethyltoluene	$C_6H_5CH_2CH_3$
86.18	2-Methylpentane	$CH_3CH(CH_3)(CH_2)2CH_3$	120.20	*p*-Ethyltoluene	$C_6H_5CH_2CH_3$
86.18	3-Methylpentane	$CH_3(CH_2)2CH(CH_3)CH_3$	120.19	1,3,5-Trimethylbenzene	$C_6H_3(CH_3)3$
68.12	Isoprene	$CH_2C(CH_3)CHCH_2$	120.20	*o*-Ethyltoluene	$C_6H_5(CH_2CH_3)$

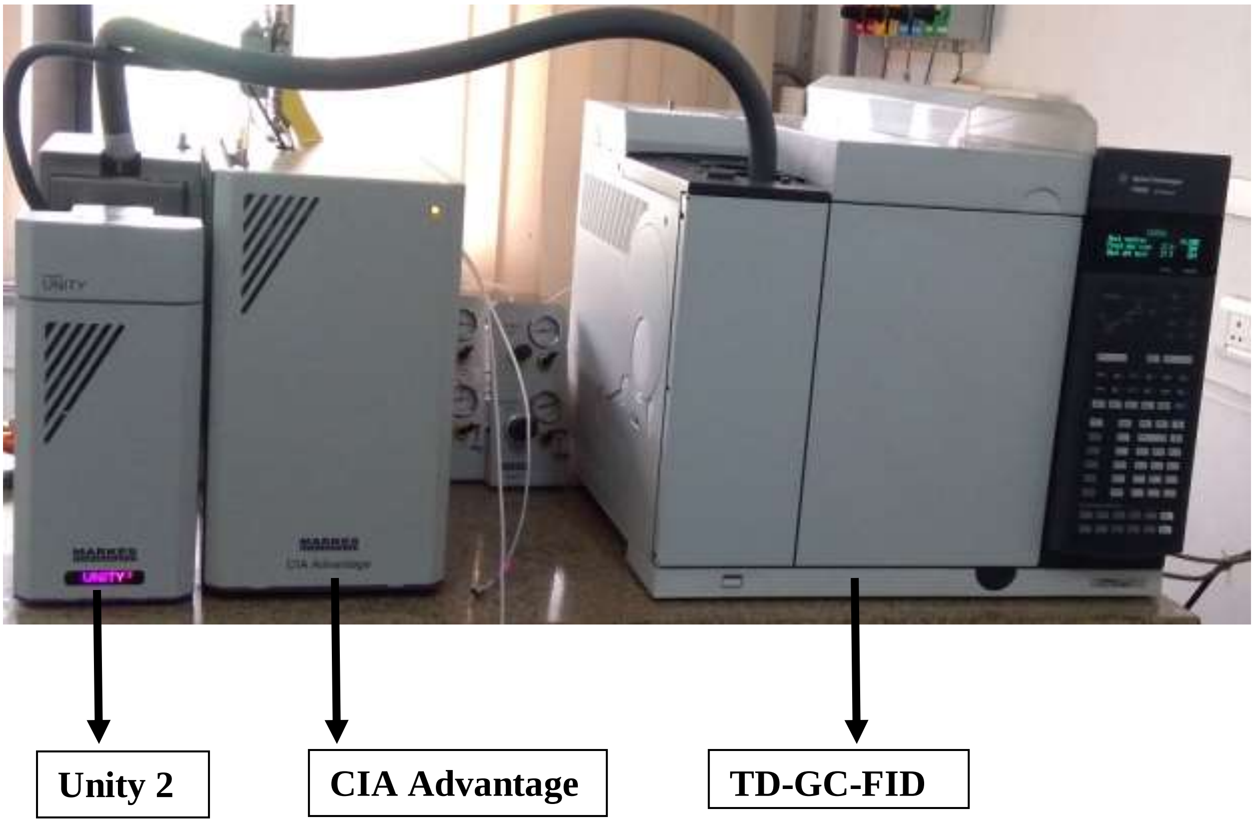
84.16	2-Methylpent-1-ene	$CH_2C(CH_3)(CH_2)2CH_3$	120.19	1,2,4-Trimethylbenzene	$C_6H_3(CH_3)3$
86.18	n-Hexane	$CH_3(CH_2)4CH_3$	142.29	Decane	$CH_3(CH_2)8CH_3$
84.16	Methylcyclopentane	$C_5H_9(CH_3)$	120.19	1,2,3-trimethylbenzene	$C_6H_3(CH_3)3$
100.2	2,4-Dimethylpentane	$CH_3CH(CH_3)CH_2CH(CH_3)CH_3$	134.22	*m*-Diethylbenzene	$C_6H_4(CH_2CH_3)2$
78.11	Benzene	(CH)6	134.22	*p*-diethylbenzene	$C_6H_4(CH_2CH_3)2$
84.16	Cyclohexane	$(CH_2)6$	156.31	Undecane	$C_{11}H_{24}$
100.2	2-Methylhexane	$CH_3CH(CH_3)CH_2)3CH_3$	170.33	Dodecane	$CH_3(CH_2)10CH_3$

Table 2.2.1 c) Dilution flows with GC and PTR-QMS standards.

	GC calibration		**PTR-QMS calibration**	
Point	**Standard gas flow (sccm)**	**Zero air flow (sccm)**	**Standard gas flow (sccm)**	**Zero air flow (sccm)**
2 ppbv	4	2000	4	1000
5 ppbv	5	1000	5	500
10 ppbv	5	500	10	500
20 ppbv	10	500	20	500

2.2.2 Instrumental details and analysis

Photograph 2.2.2 a) shows a TD-GC-FID complete setup used in this study.



Photograph 2.2.2 a) GC-FID, Unity 2 and CIA Advantage system.

2.2.2.1 Gas chromatography (Agilent Gas Chromatographs)

Gas chromatography is an analytical technique, used to separate a mixture into individual components. It is used to identify components and to measure their concentrations. Unlike physical separation methods like distillation, GC separates the components in time and after detection results in a chromatogram, where each peak represents a different component of the original mixture. The elution time is used to identify individual components and peak area to measure the components concentration. The components of a gas chromatographic system are shown in figure 2.2.2.1 a)

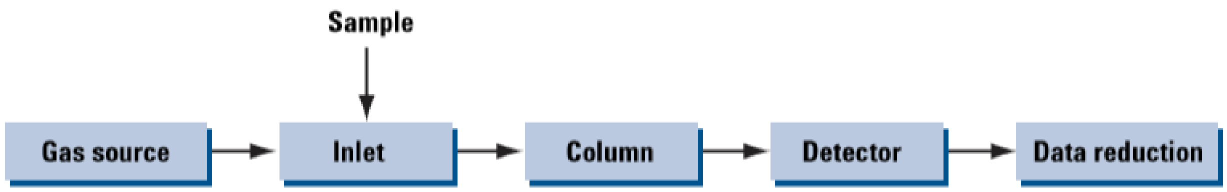


Figure 2.2.2.1 a) A chromatographic system.

A purified carrier gas source which moves the sample through the GC. A high purity carrier gas with traps for water, hydrocarbons and oxygen is recommended to get a good quality of chromatogram.

Inlet, from where sample is injected to the GC system through a sampling valve.

Column, separation of components take place in time as a function of temperature. The properties of stationary phase determines the column temperature range. The minimum temperature be the melting point and maximum be the boiling point or degradation temperature of stationary phase. So column is put inside a well-controlled oven as shown in figure 2.2.2.1 b). The oven temperature can be isothermal or programmed as shown in figure 2.2.2.2 c). Here, in this study oven temperature was programmed according to the properties of the sample mixture.

Detector, responds to the components as their electrical output gets change and gives a chromatogram as an output.

Data reduction, peak times and sizes are determined directly by a digital integrator and computer based data system.

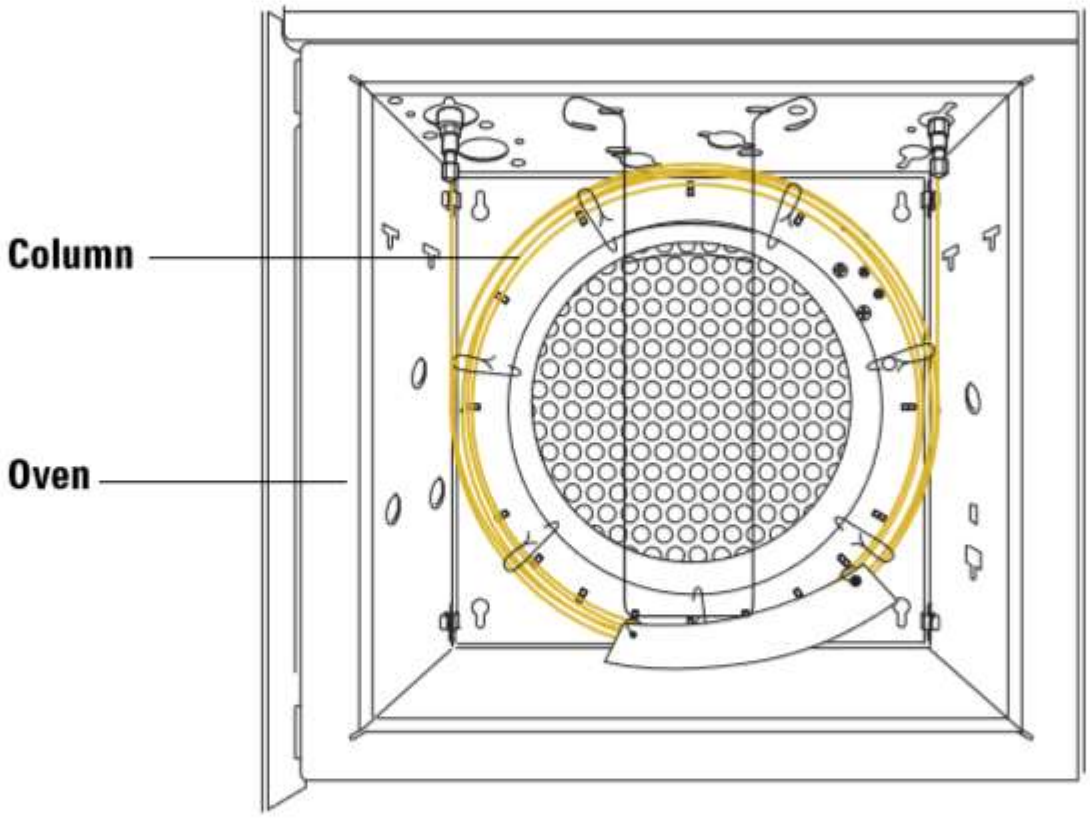


Figure 2.2.2.1 b) Column and oven.

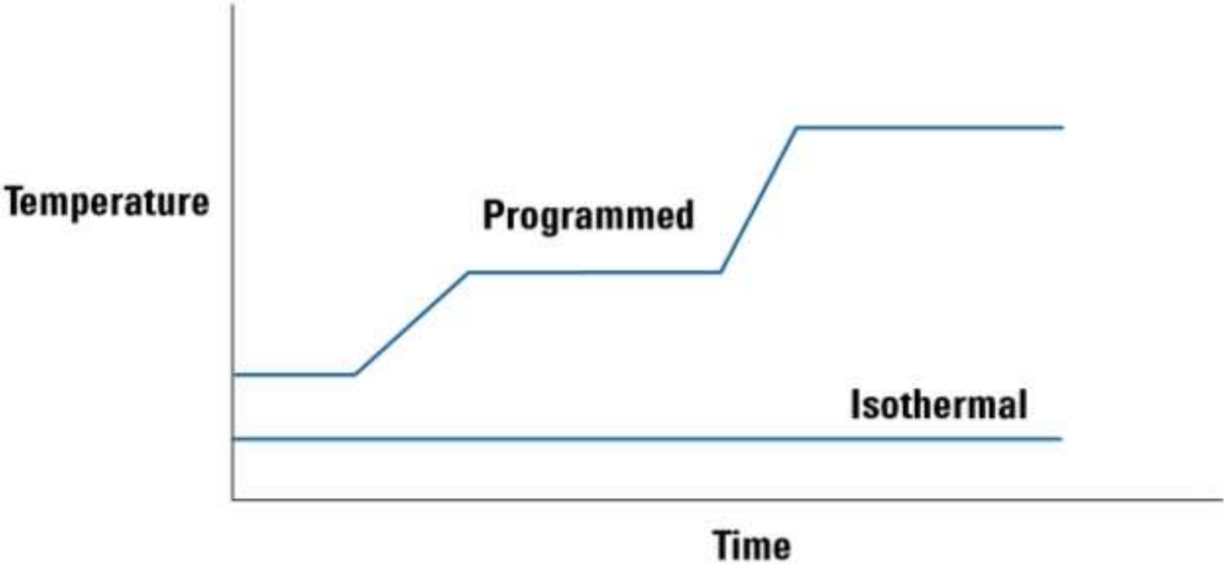


Figure 2.2.2.1 c) Oven temperature.

The components of a vaporized mixture are separated inside the column on the basis of their properties like volatility and chemical interactions with stationary phase of the column. The component with less volatility and high chemical interaction with stationary phase lacks in time than the component with high volatility and less chemical interaction with stationary phase and thus eluted first from the column and appears in the chromatogram at a lower time. Thus, separation of components take place in time.

The columns used in this study are the capillary columns, figure 2.2.2.1 d). A capillary column have no packing and is an open tube with the stationary phase coated inside the surface. Capillary columns are good for the separation of complex mixtures because they produce very narrow peaks, give a good resolution (separates peaks down to the baseline) and also a small amount of sample is required than packed columns. It's their small tubing diameter and a thin stationary phase layer that improves their efficiency and thus produces narrow peaks.

Figure 2.2.2.1 d) A capillary column.

The detector used in this study was flame ionization detector (FID). It works by burning the carbon containing material in a flame and produces a current which is amplified than when no compound is present in the air jet coming from the column and this current creates a chromatogram. The FID uses two electrodes, one where flame burns and another where ions are collected from the flame. A general design of FID is shown in figure 2.2.2.1 e).

GC-FID system used in this study was 7890B, Agilent technologies, USA and is equipped with two capillary columns, a Deans switch and two flame ionization detectors. Two columns used are (Markes international, TDTS16 and *Dettmer et al. 2002*)–

(1) Column 1, 60 m, 0.25 mm, 1 μm, dimethylpolysiloxane, C_{6+} compounds get separate here

(2) Column 2, 50 m, 0.32 mm, 8 µm, alumina PLOT, C_2 – C_5 compounds get resolve here.

Two columns are connected via a Deans switch and works together for the starting 17.5 minutes of the GC run, GC run last for 44 minutes and during this time separation of components occur and then works separately for the rest of the GC run. Both the columns temperature is programmed during the complete GC run. They start to operate at 30°C and this temperature hold for 12 minutes followed by a 5°C/minute rise in the temperature to 170°C and this temperature was hold for 1 minute and finally temperature was raised at 15°C/minute rate and reached a value 200°C and hold for 1 minute. After this GC run

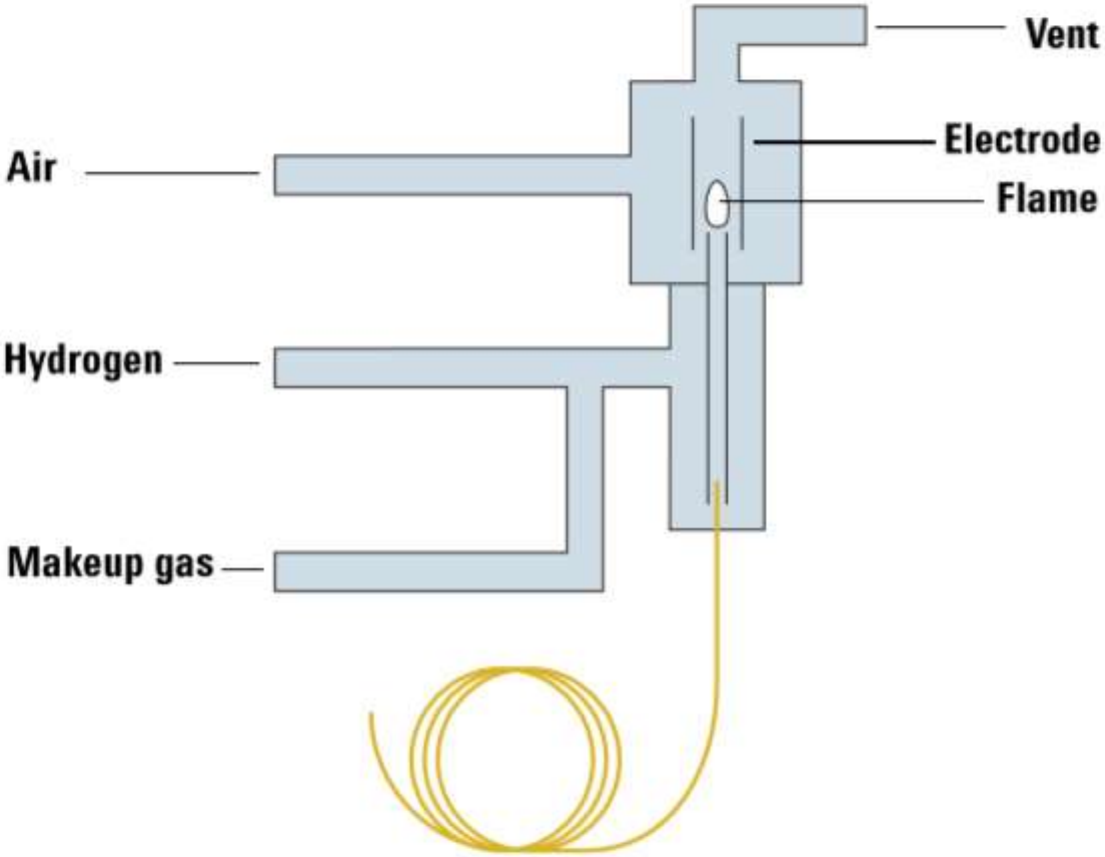


Figure 2.2.2.1 e) Flame ionization detector.

get over and a chromatogram was obtained. A standard chromatogram obtained with TD-GC-FID is shown in figure 2.2.2.1 f). The sample was injected to the column 1 firstly, at 30°C this column is unable to separate the $C_2 – C_5$ compounds and passed to the column 2 through the Deans switch and goes to one of the FID. For the first 17.5 minutes of the run Deans switch work in this way and after this the compounds eluting from column 1 are C_{6+} and are well resolved and goes to another FID. From this point onwards two chromatograms are produced in parallel: the C_{6+} compounds from the column 1 labelled FID 1 and $C_2 – C_5$ compounds from the column 2 labelled FID 2.

The isoprene detection limit of the GC-FID system is 4ppt and measurement uncertainty < 6%.

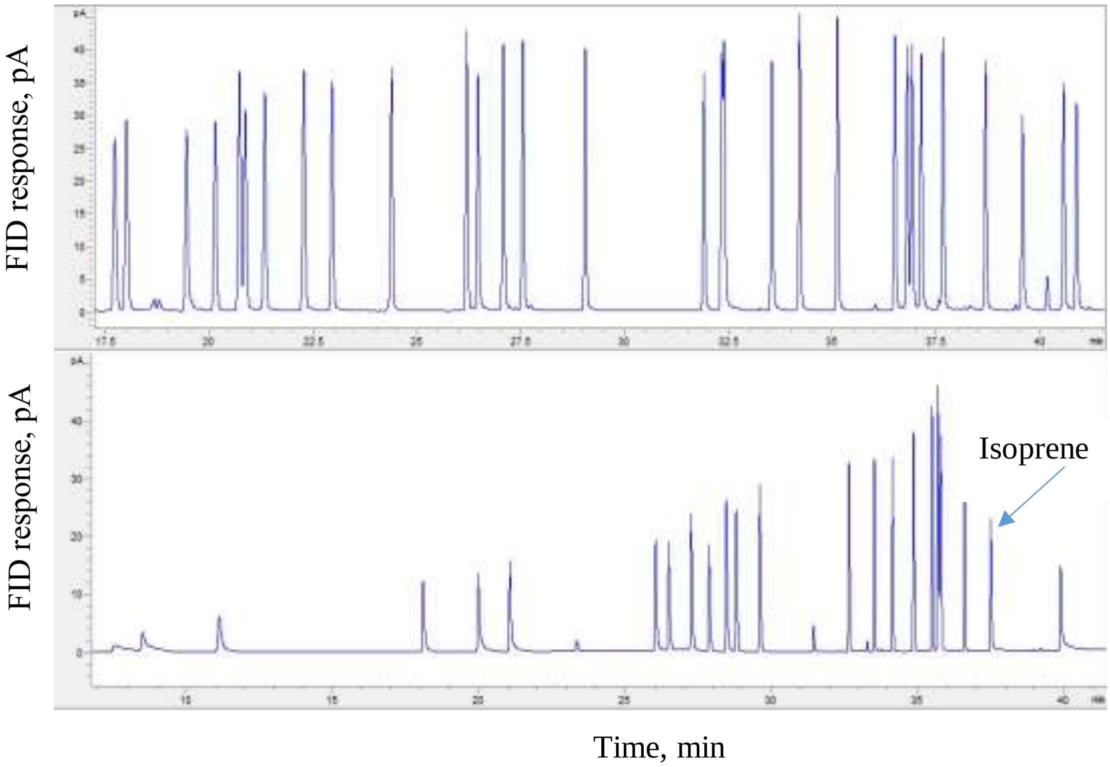


Figure 2.2.2.1 f) Standard chromatogram obtained with TD-GC-FID.

2.2.2.2 Unity 2

Unity 2 instrument is used for the sample pre-concentration. It consists of a cold trap which operates thermally having temperature of functioning from -30°C to 320°C. It consists of three adsorbent materials which are arranged in the order of their absorptivity power from lower to higher. The three adsorbents materials are tenax (non-polar adsorbent, C# > 4), carboxen (non-polar adsorbent, sulfonated polymers, $C_2 – C_5$) and carbosieves (non-polar adsorbent, polyvinyl chloride, $C_2 – C_5$), (*Dettmer et al. 2002*). It is the cold trap where pre-concentration of sample happens. The pre-concentration time is 50 minutes and during pre-concentration cold trap works at -30°C. The gaseous sample pre-concentrates on the cold trap for 50 minutes at -30°C. Any water and oxygenated compound is removed by Nafion dryer via which sample goes to cold trap. Sampling was followed by post-sampling purge (10 minutes) and trap purge (5 minutes) which are followed by thermal desorption of the sample as cold trap temperature increases from -30°C to 320°C within a period of 1 minute and was transferred to the inlet of the GC-FID system. Figure 2.2.2.2 a) shows a cold trap with its adsorbent materials.

2.2.2.3 CIA Advantage

CIA Advantage is a 14 port system through which sample injection takes place. It consists of a Nafion dryer, use of which was explained in section 2.2.2.2 Unity 2. Through any one of the ports sample goes to the Nafion dryer and after becoming water and oxygenated free goes to the Unity setup for pre-concentration process on the cold trap.

Chapter 3

Results and discussion

BVOCs were quantified with TD-GC-FID and PTR-QMS and water content and CO_2 assimilation was quantified with CRDS. On looking at the fragmentation pattern obtained from PTR-QMS and the retention time from TD-GC-FID it was found that isoprene is the major BVOC emitted by *Populus deltoides* and monoterpenes of mass 81 and 137 were also observed in trace amount. About methanol, acetone, methyl vinyl ketone (MVK) and methyl ethyl ketone (MEK) nothing can be clearly said because these compounds were not properly scrubbed in the ambient air. Monsoon season has data points from 08/08/2018, 10:40 to 15/08/2018, 17:52 and post-monsoon season has data points from 28/11/2018, 18:08 to 08/12/2018, 00:00. During post-monsoon due to some instrumental problem in PTR-QMS data points were not available for the following time periods: 29/11/2018, 16:08 - 16:20; 30/11/2018, 13:08 - 13:40; 01/12/2018, 12:52 - 14:12, 16:52 - 18:08; 02/12/2018 17:20 - 20:36; 04/12/2018, 07:12 - 10:20, 21:44 - 21:56; 05/12/2018, 15:08 - 19:20, 21:08 - 22:48; 06/12/2018, 02:52 – 07/12/2018, 09:48; 07/12/2018, 11:04 – 15:32. Background was done during both the seasons to get an idea how much in-flux of BVOC was being provided to the cuvette system, following were the timings of background for two seasons: 15/08/2018, 22:40 – 16/08/2018, 14:24 for monsoon season and 02/12/2018, 13:24 – 13:44; 03/12/2018, 00:00 – 00:16, 11:44 – 12:00, 16:52 – 17:12; 05/12/2018, 09:16 – 09:28 for post-monsoon season.

Figure 3 a). shows the isoprene mixing ratio along with monoterpenes mixing ratio, leaf temperature and photosynthetically active radiation (PAR) for monsoon and post-monsoon season**.** The color code of axis label is same as of the color code of the plot. The maximum isoprene mixing ratio obtained during both seasons is shown by shaded rectangles, red shade for monsoon season and blue shade for post-monsoon season.

During monsoon season, Sun rose at 06:00 hour and set at 19:00 hour. With **PTR-QMS**, maximum isoprene mixing ratio observed was 638.60 ppbv on 09/08/2018, 08:44 hour having corresponding leaf temperature and PAR value of 46.95°C and 1070.2 μmolm^{-2}s^{-1} respectively. Background isoprene mixing ratios were measured on 16/08/2018 having maximum and minimum isoprene mixing ratio value of 5.1 ppbv at 07:28 hour and 0.5 ppbv at 10:16 hour respectively. With **TD-GC-FID,** maximum isoprene mixing ratio observed was 443.1 ppbv on 10/08/2018, 09:24 hour having corresponding leaf temperature and PAR value of 41.5°C and 1084.4 μmolm^{-2}s^{-1} respectively. A decrease in isoprene mixing ratio, leaf temperature and PAR were observed during 12/08/2018 and 1308/2018 due to rain fall event occurred during these two days at times 12/08/2018, 07:00 – 11:00 and 13/08/2018, 01:00 – 07:00 respectively. And, maximum monoterpene emission ratio obtained was 10.47 ppbv.

During **post-monsoon** season, Sun rose at 07:00 hour and set at 17:00 hour. With **PTR-QMS**, maximum isoprene mixing ratio observed was 54.64 ppbv on 01/12/2018, 10:24 hour having corresponding leaf temperature and PAR values of 33.23°C and 827.9 μmolm^{-2}s^{-1} respectively. Background isoprene mixing ratios were measured on 16/08/2018 having maximum and minimum isoprene mixing ratio value of 0.65 ppbv at 11:50 hour and 0.03 ppbv at 17:08 hour respectively. With **TD-GC-FID**, maximum isoprene mixing ratio observed was 34.6 ppbv on 30/11/2018, 10:40 having corresponding leaf temperature and PAR values of 34.7°C and 751.7 μmolm^{-2}s^{-1} respectively. And, maximum monoterpene emission ratio obtained was 5.18 ppbv.

From the figure 3 a) it can be clearly seen that isoprene mixing ratio is a function of leaf temperature and PAR and low background values confirms a good quality of silica and charcoal used to scrub the ambient air from moisture and isoprene.

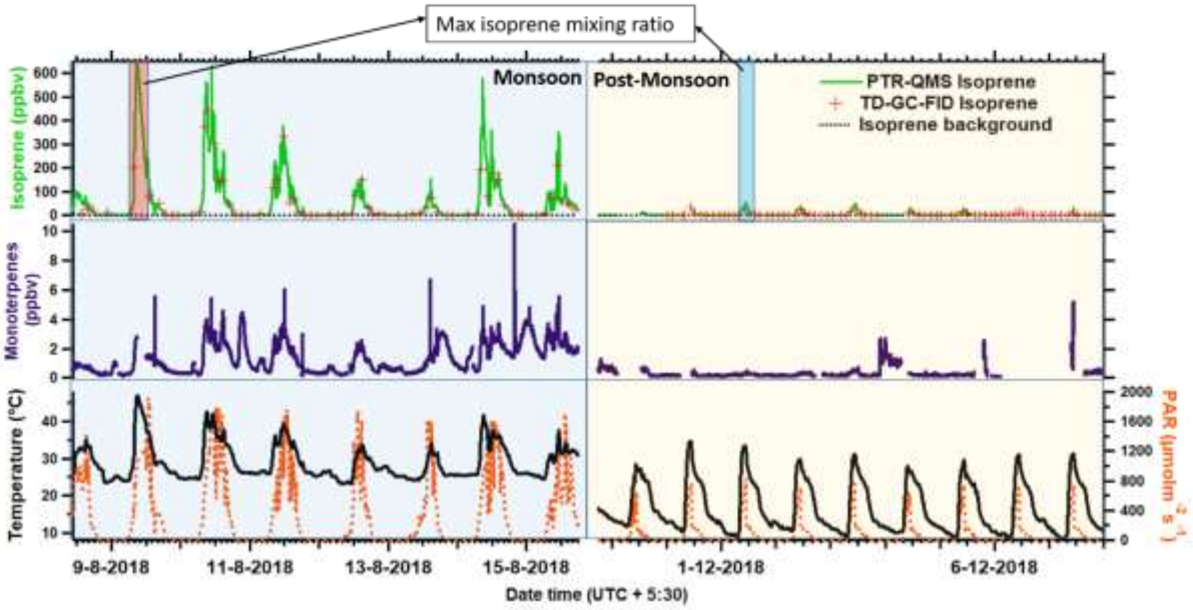


Figure 3 a) Isoprene mixing ratio (PTR-QMS and TD-GC-FID) along with isoprene background, monoterpenes mixing ratio (PTR-QMS), photosynthetically active radiation and leaf temperature.

Table 3 a) Max. isoprene mixing ratio with max. leaf temperature for both monsoon and post-monsoon seasons.

Season	Max. isoprene mixing ratio (ppbv)	Max. temperature (°C)	Date and time
Monsoon	638.60	46.95	09/08/2018, 08:44
Post-monsoon	54.64	33.23	01/12/2018, 10:24

Figure 3 b). shows the diel profile of isoprene mixing ratio with leaf temperature and photosynthetically active radiation for monsoon and post-monsoon season. The color code of axis label is same as of the color code of the plot. During **monsoon season**, leaf temperature dominated the isoprene emission trend more than PAR. Isoprene emission started as Sun rises at 06:00 hour, attained a maximum value of 162.0 ppbv at 08:00 hour having corresponding leaf temperature and PAR values of 32.8°C and 531.9 μmolm^{-2}s^{-1} respectively and then went to a minimum value of ≈ 1 ppbv as Sun sets at 19:00 hour. The black dotted line represents the background isoprene mixing ratio having a maximum value of 3.8 ppbv.

During **post-monsoon season**, both the leaf temperature and PAR defined the ascending order of the isoprene emission plot but in the descending trend PAR is the dominate factor than the leaf temperature. Isoprene emission started as Sun rises at 07:00 hour, attained a maximum value of 26.8 ppbv at 10:00 hour having corresponding leaf temperature and PAR values of 30.8°C and 650.9 μmolm^{-2}s^{-1} respectively and then went to a minimum value of ≈ 0.4 ppbv as Sun sets at 17:00 hour. The black dotted line represents the background isoprene mixing ratio having a maximum value of 2.0 ppbv.

On looking at the diel profile of monsoon season PAR got a maxima value at 13:00 hour but isoprene maxima was obtained at 08:00 hour which was due to position the dynamic branch cuvette system and Decagon device and causing the different availability of Sunlight to both of them. While, during post-monsoon season both PAR and isoprene maxima were obtained at 10:00 hour which was due to the same availability of Sunlight to plant chamber and Decagon device.

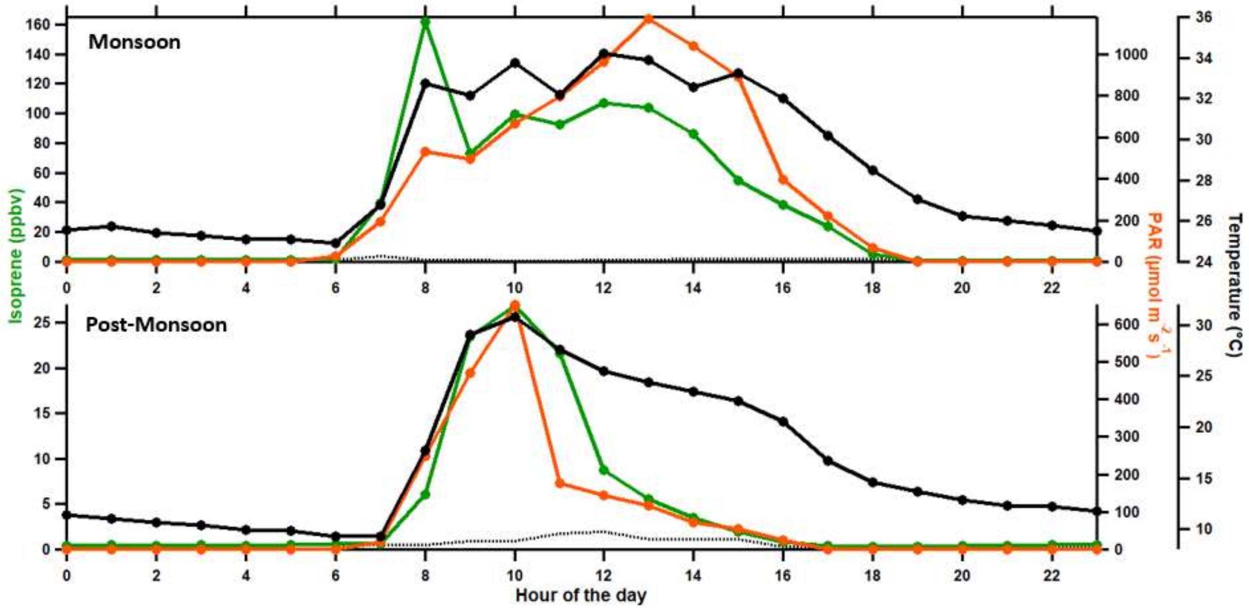
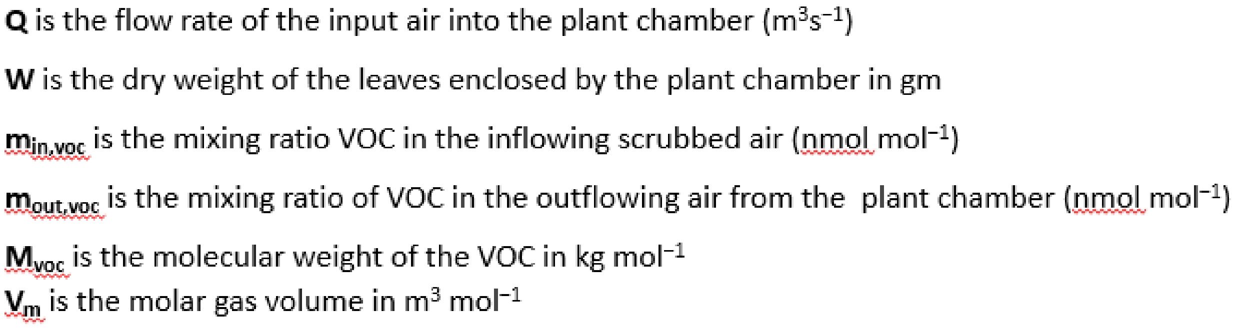


Figure 3 b) Diel profile of isoprene mixing ratio (PTR-QMS) along with isoprene background leaf temperature and photosynthetically active radiation.

Hourly isoprene flux value was obtained by equation (*Sinha et al. 2007*):

$$\mathbf{EF_{VOC}}\ (\mu g\ g^{-1}\ hr^{-1}) = \frac{\mathbf{m_{out,voc}} - \mathbf{m_{in,voc}}\ (nmol\ mol^{-1})}{\mathbf{V_m}(m^3\ mol^{-1})} \times \frac{\mathbf{M.W.}\,(g\ mol^{-1})\ \times \mathbf{Q}\ (m^3\ hr^{-1})}{\mathbf{W}\ (g)}$$

where,



Q is the flow rate of the input air into the plant chamber ($m^3 s^{-1}$)

W is the dry weight of the leaves enclosed by the plant chamber in gm

$\mathbf{m_{in,voc}}$ is the mixing ratio VOC in the inflowing scrubbed air ($nmol\ mol^{-1}$)

$\mathbf{m_{out,voc}}$ is the mixing ratio of VOC in the outflowing air from the plant chamber ($nmol\ mol^{-1}$)

$\mathbf{M_{voc}}$ is the molecular weight of the VOC in kg mol^{-1}

$\mathbf{V_m}$ is the molar gas volume in $m^3\ mol^{-1}$

Figure 3 c). shows hourly isoprene emission flux for both the seasons monsoon and post-monsoon. The color code in the plot corresponds to the respective axis label color code. The plot relates different parameters like isoprene flux (µg g^{-1} hr^{-1}), leaf temperature (°C), PAR (µmol$m^{-2}s^{-1}$) and soil moisture (m^3m^{-3}). **During monsoon** period a maximum isoprene flux value of 67.79 µg g^{-1} hr^{-1} in terms of leaf dry weight and 11.45 nmol m^{-2} s^{-1} in terms of leaf area respectively was obtained on 08/09/2018 at 08:00 am having corresponding leaf temperature and PAR value of 42.68°C and 896.77 µmol$m^{-2}s^{-1}$ respectively. An average of isoprene flux obtained was 13.66 µg g^{-1} hr^{-1} and 2.31 nmol m^{-2} s^{-1} respectively in terms of leaf dry weight and leaf area. With **TD-GC-FID**, maximum isoprene emission flux observed was 58.35 µg g^{-1} hr^{-1} on 10/08/2018, 09:00 having corresponding leaf temperature and PAR values of 40.90°C and 1091.68 µmol$m^{-2}s^{-1}$ respectively. And, maximum monoterpenes flux obtained was 1.23 µg g^{-1} hr^{-1} in terms of leaf dry weight and 0.10 nmol m^{-2} s^{-1} in terms of leaf area respectively.

During post-monsoon period a maximum isoprene flux of 18.02 µg g^{-1} hr^{-1} in terms of leaf dry weight and 6.02 nmol m^{-2} s^{-1} in terms of leaf area respectively was obtained on 01/12/2018 at 10:00 am having corresponding leaf temperature and PAR value of 33.08°C and 677.53 µmol$m^{-2}s^{-1}$ respectively. An average of isoprene flux obtained was 4.51 µg g^{-1} hr^{-1} in terms of leaf dry weight and 1.51 nmol m^{-2} s^{-1} in terms of leaf area respectively. With **TD-GC-FID**, maximum isoprene emission flux observed was 15.86 µg g^{-1} hr^{-1} on 30/11/2018, 12:00 having corresponding leaf temperature and PAR values of 26.29°C and 148.77 µmol$m^{-2}s^{-1}$ respectively. And, maximum of monoterpenes flux obtained was 2.43 µg g^{-1} hr^{-1} in terms of leaf dry weight and 0.41 nmol m^{-2} s^{-1} in terms of leaf area respectively.

From figure 3 c) a rise in soil moisture is observed during 12/08/2018 to 14/08/2018 period for monsoon season which is accounted as a period of increased rain fall. No soil moisture data was available for the post-monsoon season because Decagon device was not working during that time period. Leaf temperature and PAR are the defining factors for the isoprene emission from *Populus deltoides* during both seasons but post-monsoon season has negligible isoprene emission in comparison to monsoon season and this behavior can be accounted as post-monsoon is a fall season and leaves are yellowish in color and plant was shading it's leaves thus less number of leaves were contributed to the total isoprene flux value. Also, during mature stage leaves emit more isoprene than during old stage (*Sharkey et al. 2008*).

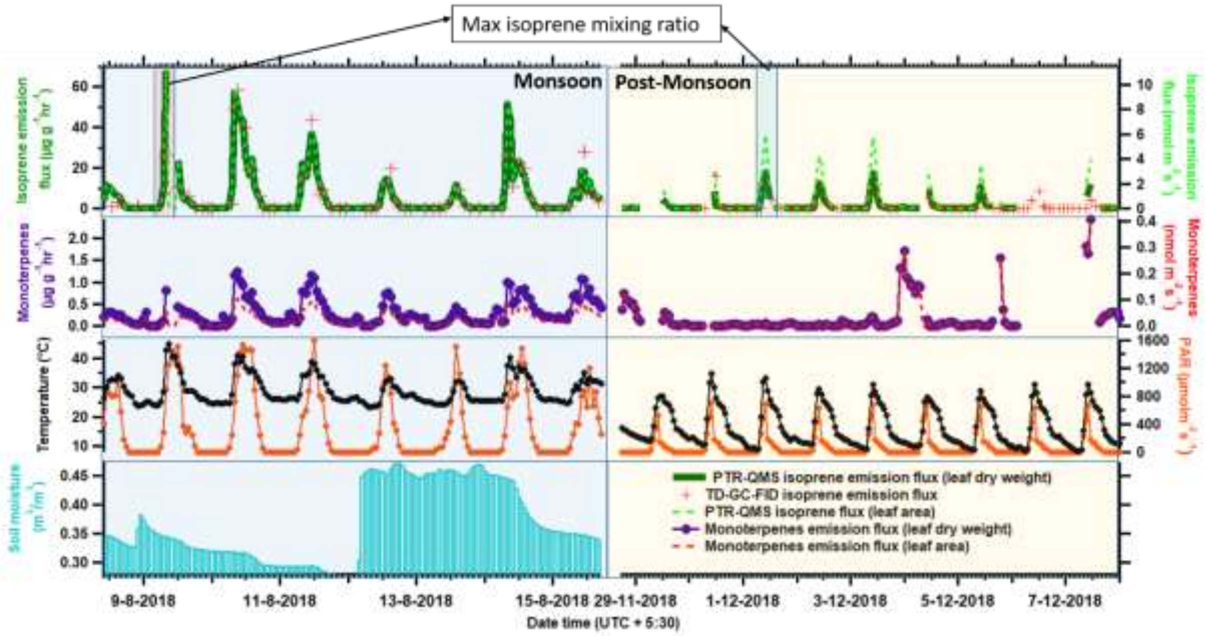
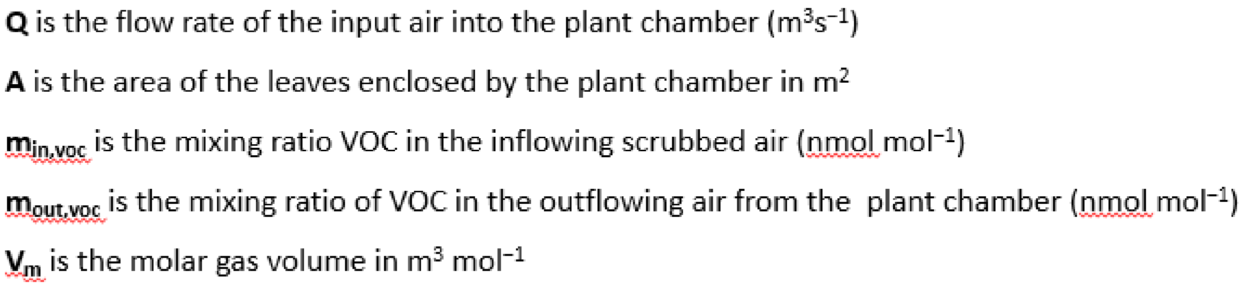


Figure 3 c) Isoprene emission flux (PTR-QMS and TD-GC-FID), monoterpenes emission flux (PTR-QMS) along with leaf temperature, photosynthetically active radiation and soil moisture.

Isoprene flux is calculated in terms of weight of dry leaves and the molecular weight of isoprene. To get the isoprene flux in terms of leaf area the above equation is modified to-

$$\mathbf{EF}_{voc}\ (\mathrm{nmol\ m^{-2}\ s^{-1}}) = \frac{\mathbf{m}_{out,voc} - \mathbf{m}_{in,voc}\ (\mathrm{nmol\ mol^{-1}})}{\mathbf{V_m}(\mathrm{m^3\ mol^{-1}})} \times \frac{\mathbf{Q}\ (\mathrm{m^3\ hr^{-1}})}{\mathbf{A}\ (\mathrm{m^2})}$$

where,



Q is the flow rate of the input air into the plant chamber ($m^3 s^{-1}$)

A is the area of the leaves enclosed by the plant chamber in m^2

$m_{in,voc}$ is the mixing ratio VOC in the inflowing scrubbed air (nmol mol^{-1})

$m_{out,voc}$ is the mixing ratio of VOC in the outflowing air from the plant chamber (nmol mol^{-1})

V_m is the molar gas volume in m^3 mol^{-1}

and calculated maximum isoprene emission flux for the two seasons is tabulated in table 3 c).

Leaf area index (LAI) value for *Populus deltoides* using field sampling method is 4.19 (*Antonarakis et al. 2010*), average isoprene flux during monsoon and post-monsoon seasons are 0.06 nmol m^{-2} s^{-1} and 0.02 nmol m^{-2} s^{-1} respectively and area covered by *Populus deltoides* in India is 2700 km^2 thus total isoprene flux over India due to *Populus deltoides* can be calculated as-

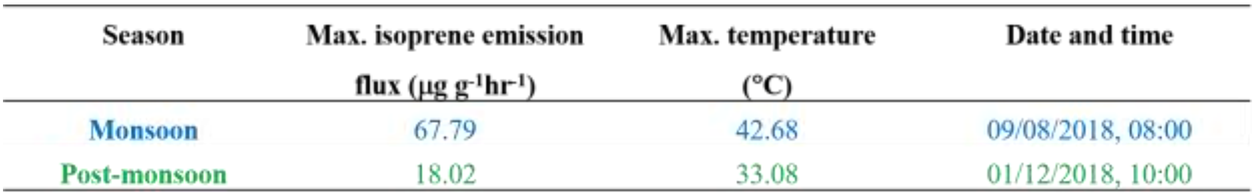
LAI × isoprene flux × Area of *Populus deltoides*

In India, monsoon season lasts for four months so total isoprene flux over India due to *Populus deltoides* is – 4.19×2.31 nmol m^{-2} s^{-1} $\times 2700$ km^2 $= 4.19 \times (2.31 \times 60.05 \times 3456000)$ ngC m^{-2} yr^{-1} $\times 2700 \times 10^6$ m^2 $= 1.41 \times 10^{17}$ ngC yr^{-1} = **5.42 GgC yr^{-1}**.

Similarly, for the post-monsoon season which also lasts for the four months in India so total isoprene flux over India is –

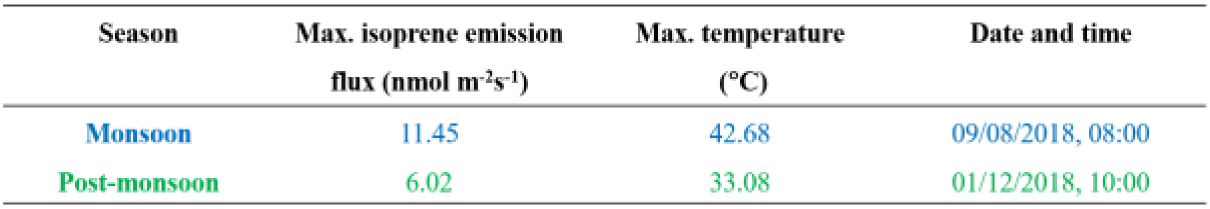
4.19×1.51 nmol m^{-2} s^{-1} $\times 2700$ km^2 $= 4.19 \times (1.51 \times 60.05 \times 3456000)$ ngC m^{-2} yr^{-1} $\times 2700 \times 10^6$ m^2 = **3.55 Gg yr^{-1}**.

Table 3 b) Max. isoprene emission flux with max. leaf temperature for both monsoon and post-monsoon seasons in terms of leaf dry weight.



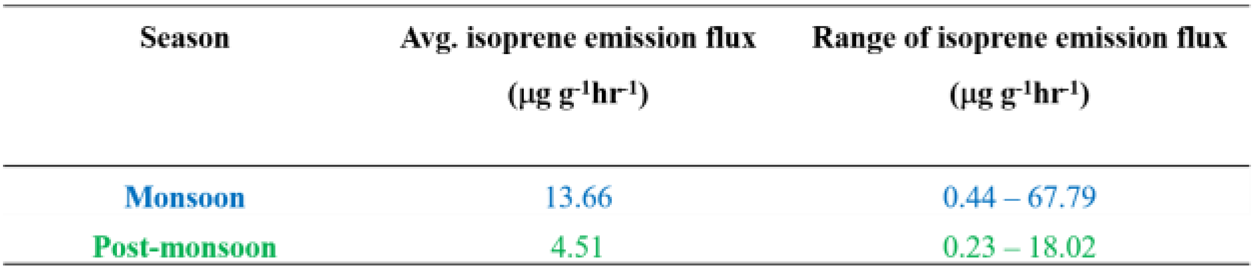
Season	Max. isoprene emission flux (μg $g^{-1}hr^{-1}$)	Max. temperature (°C)	Date and time
Monsoon	67.79	42.68	09/08/2018, 08:00
Post-monsoon	18.02	33.08	01/12/2018, 10:00

Table 3 c) Max. isoprene emission flux with max. leaf temperature for both monsoon and post-monsoon seasons in terms of leaf area.



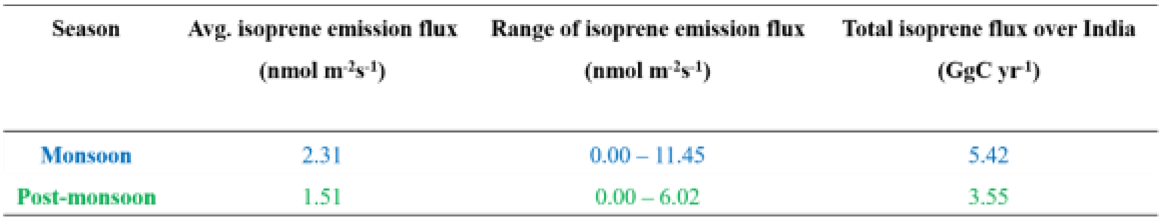
Season	Max. isoprene emission flux (nmol m^{-2}s^{-1})	Max. temperature (°C)	Date and time
Monsoon	11.45	42.68	09/08/2018, 08:00
Post-monsoon	6.02	33.08	01/12/2018, 10:00

Table 3 d) Average and range of isoprene emission flux for both monsoon (07:00 AM to 05:00 PM) and post-monsoon (08:00 AM to 04:00 PM) seasons in terms of leaf dry weight, including only day hours.



Season	Avg. isoprene emission flux (µg g^{-1}hr^{-1})	Range of isoprene emission flux (µg g^{-1}hr^{-1})
Monsoon	13.66	0.44 – 67.79
Post-monsoon	4.51	0.23 – 18.02

Table 3 e) Average, range of isoprene emission flux, total isoprene flux over India for both monsoon (07:00 AM to 05:00 PM) and post-monsoon (08:00 AM to 04:00 PM) seasons in terms of leaf area, including only day hours.



Season	Avg. isoprene emission flux (nmol m^{-2}s^{-1})	Range of isoprene emission flux (nmol m^{-2}s^{-1})	Total isoprene flux over India (GgC yr^{-1})
Monsoon	2.31	0.00 – 11.45	5.42
Post-monsoon	1.51	0.00 – 6.02	3.55

Figure 3 d). shows diel profile of isoprene emission flux for both the seasons monsoon and post-monsoon. The color code in the plot corresponds to the respective axis label color code. The plot relates different parameters like isoprene flux (µg g^{-1} hr^{-1}), leaf temperature (µmol/m^{2}s) with respect to hour of the day (local time). **During monsoon**, Sun rose at 6 am and set at 6 pm. Ideally, isoprene flux follow the trend of maximum at noon and goes to zero after sunset and before sunrise. And, as Sun rose at 6 am isoprene flux started to rise from zero, reaches a maximum of 22.17 µg g^{-1} hr^{-1} at 8 am and became zero as Sun sets at 6 pm. A maximum PAR value of 1196.85 µmol/m^2s was obtained at 13:00 hour and a maximum leaf temperature of 34.51°C at 12:00 hour. The maximum isoprene flux at 08:00 hour and PAR at 13:00 hour can be explained in terms of the different position of the dynamic branch cuvette system and decagon device and thus difference in the availability of the Sunlight to the two. On looking at the plot isoprene flux can be correlated more closely with leaf temperature than PAR.

During post-monsoon, Sun rose at 7 am and set at 5 pm. Here, a maximum of isoprene flux value of 11.68 µg g^{-1} hr^{-1} was obtained at 10:00 hour and zero after sunset and before sunrise which can be correlated to the leaf temperature which also has a maximum value of 30.26°C at 10:00 hour. Both the leaf temperature and PAR defined the ascending order of the isoprene emission plot but in the descending trend PAR is the dominate factor than the leaf temperature.

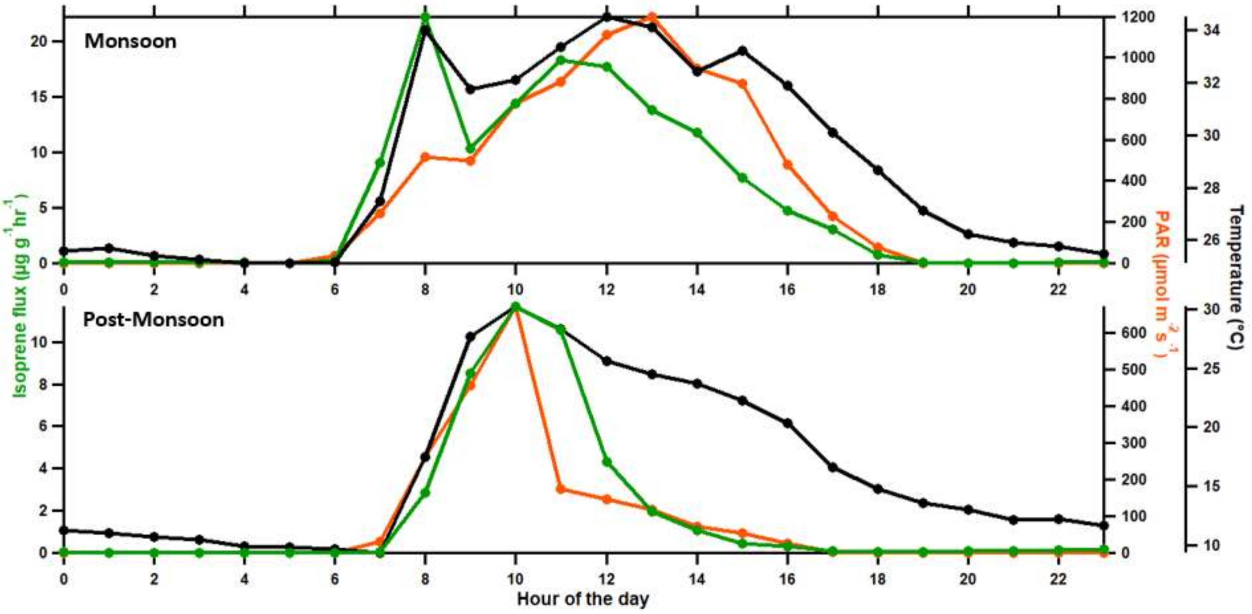
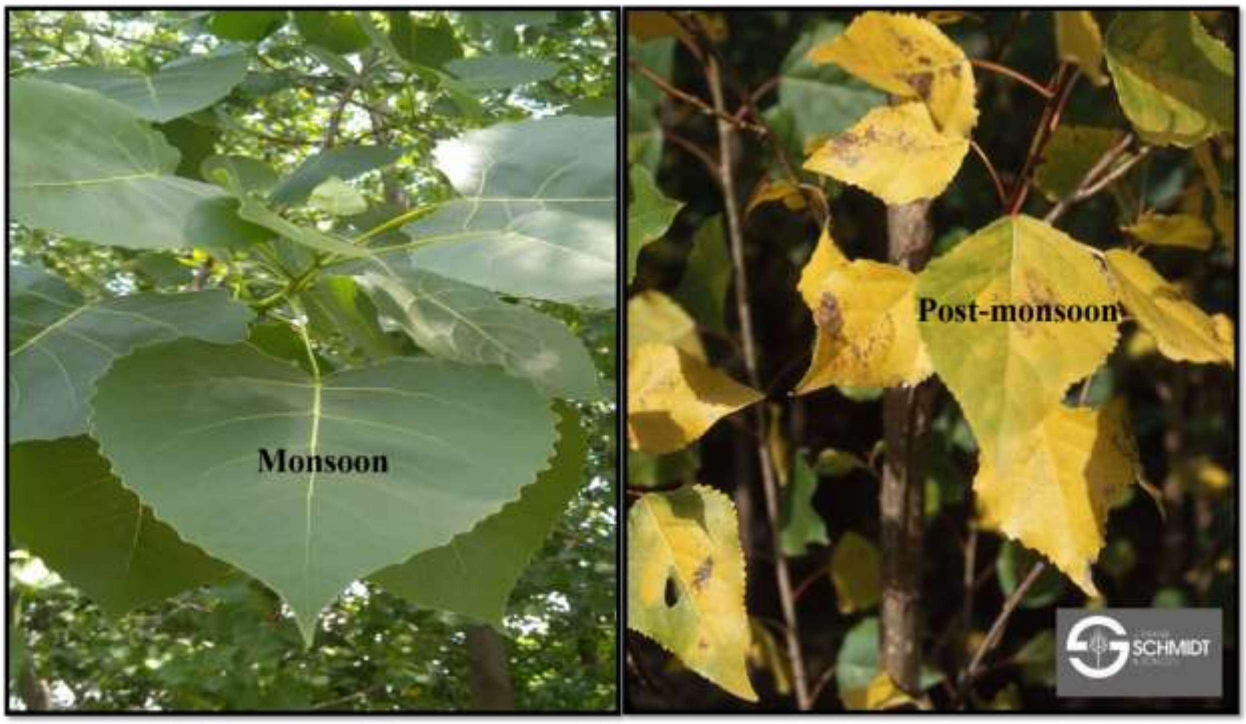


Figure 3 d) Diel profile of isoprene emission flux (PTR-QMS) along with leaf temperature and photosynthetically active radiation.

Both PAR and leaf temperature are the defining factors for the isoprene emission but post-monsoon is a fall season and *Populus deltoides* is a deciduous species, leaves were yellowish in color and also leaves were shading thus these two factors are also responsible for the low isoprene emission during post-monsoon season. Photograph 3 a) shows the leaf form for both seasons.



Photograph 3 a) *Populus deltoides* leaves during monsoon and post-monsoon (https://www.skyscrapercity.com) seasons respectively.

A quantitative information of leaf temperature and photosynthetically active radiation dependence on isoprene flux can be obtained from figure 3 e). **Figure 3 e).** shows a correlation between isoprene flux (µg g^{-1} hr^{-1}), leaf temperature (°C) and photosynthetically active radiation (µmol/m^2s). In the plot, circle and square markers represents the monsoon and post-monsoon data points respectively and green and red line showing their best fit. The black line shows a best fit of combined data for the seasons. **Figure 3 eI.)** a linear fit was obtained between isoprene flux and photosynthetically active radiation for monsoon, post-monsoon and for the merged data of the two seasons with an R value of 0.65, 0.78 and 0.70 respectively and with a slope value of 0.02 ± 0.00, 0.02 ± 0.00 and 0.02 ± 0.00 respectively. On looking at R value of the two seasons it can be concluded that during post-monsoon plant's isoprene emission capacity shows more dependence on PAR than during monsoon season. **Figure 3 eII.)** shows isoprene emission flux, PAR and leaf temperature on y-axis, x-axis and z-axis respectively. The markes are colored according to the leaf temperature value and color scale shows the leaf temperature value. From the plot it is clear that maximum isoprene flux is obtained at maximum leaf temperature but at moderate values of PAR. **Figure 3 eIII.)** a power fit plot was obtained for the monsoon, post-monsoon seasons and for the merged data of the two seasons with a power of dependency 7.94 ± 0.62, 8.80 ± 321 and 7.92 ± 0.44 respectively between isoprene flux and leaf temperature. From the power dependency it is clear that plant shows a more leaf temperature dependency for isoprene emission flux during post-monsoon season than during monsoon season. The merged best fit line shows more alignment towards monsoon season than post-season. **Figure 3 eIV)** shows isoprene emission flux, leaf temperature and photosynthetically active radiation on y-axis, x-axis and z- axis. The markers are colored according to the PAR value where the color scale shows the PAR value. From the plot it can be observed that at maximum leaf temperature maximum isoprene flux was observed whereas at moderate values of photosynthetically radiation maximum isoprene flux was observed same result as obtained from the figure 3 eII). Isoprene emission flux shows a linear dependence on PAR whereas as a power of 8 dependency on leaf temperature thus for the *Populus deltoides* isoprene emission is decided more by leaf temperature than by PAR.

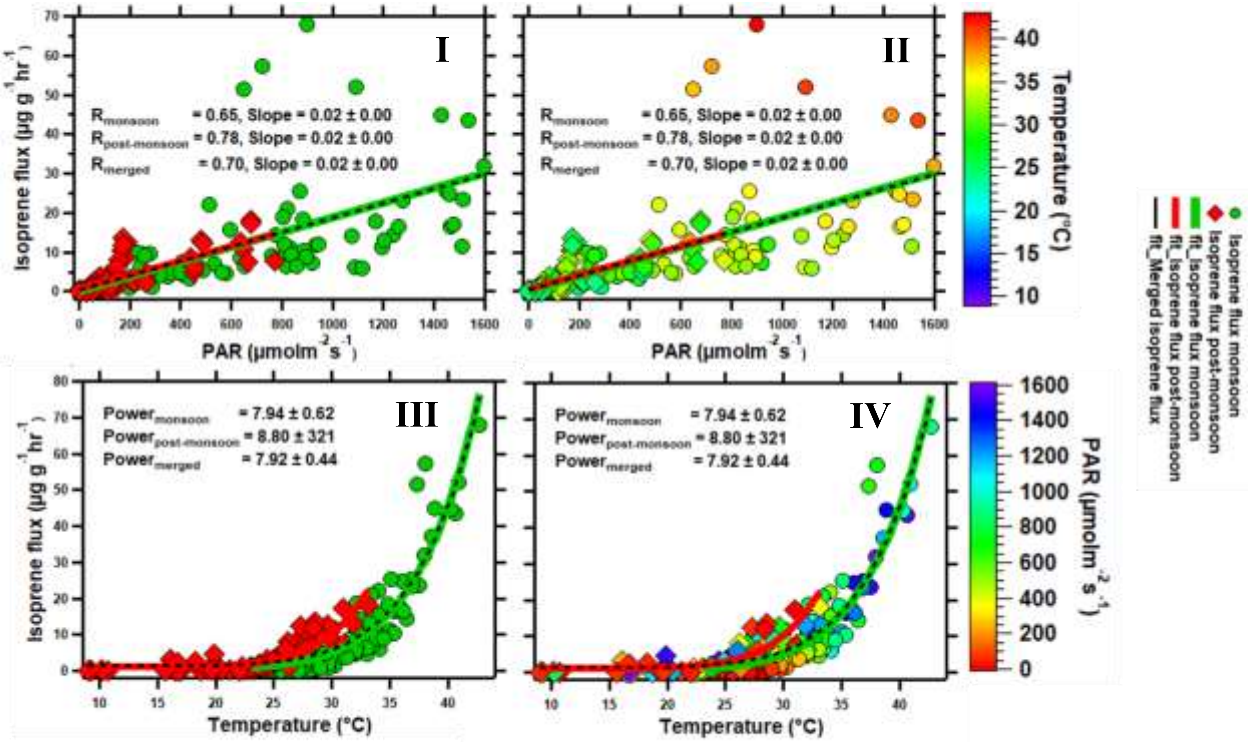


Figure 3 e) Isoprene emission flux (PTR-QMS) along with leaf temperature and PAR for both monsoon and post-monsoon seasons during dayhours.

To see how good was measured isoprene flux, measured isoprene flux is plotted against modeled isoprene flux. The equation used to determine the modeled isoprene flux is:

f(PAR,Temp.) = a + b*PAR)+ c*exp(d*Temp.), where, f = modeled isoprene flux and value of co-efficients used are given in **Table 3 f)**.

Table 3 f) Co-efficient values, used in modeled isoprene flux equation for both the seasons.

Season	a	b	c	d
Monsoon	0.48	0.02	0.02	0.19
Post-monsoon	0.71	0.02	0.02	0.21

The correlation between modeled isoprene flux and measured isoprene flux is shown in **figure 3 f).** The plot shows correlation for both monsoon, post-monsoon seasons and for the merged data of both the seasons where data points are depicted with circle and square markers for monsoon and post-monsoon season and the best fit was shown for the monsoon, post-monsoon and merged data of both the seasons having an R value of 0.92 and slope 0.84 ± 0.03, 0.90 and 0.80 ± 0.05 and 0.92 and 0.84 ± 0.02 respectively.

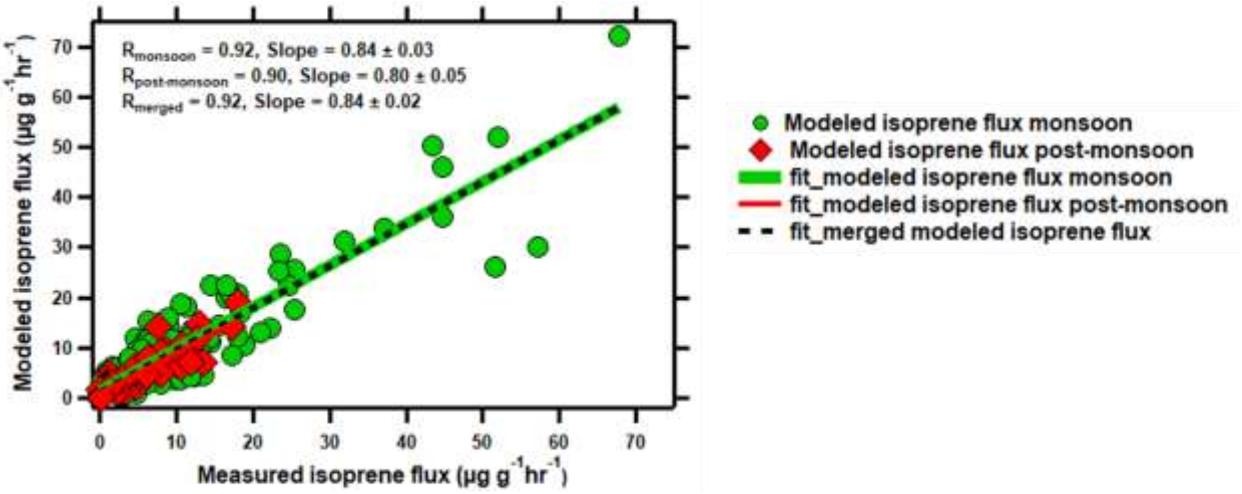


Figure 3 f) Modeled isoprene flux v/s measured isoprene flux (PTR-QMS), only day hours included.

Plants in-take CO_2 for photosynthesis and produce energy in the form of glucose. Isoprene synthesis and photosynthesis process competes with each other. So, CO_2 assimilation flux is a good idea to get information about how much carbon is being converted to isoprene and how much is stored as energy. **Figure 3 g)** shows a correlation between cumulative isoprene flux and cumulative assimilation CO_2 flux for both the monsoon and post-monsoon seasons with circle and square markers and their best fits with green and red lines having an R value 0.91 and 0.68 and slope value of 0.67 ± 0.15 and 0.28 ± 0.04 respectively. The black line represents the best fit of the merged data of both seasons having an R and slope value of 0.32 and 0.67 ± 0.15. During monsoon season a good correlation was observed that more carbon conversion took place to isoprene than during post-monsoon season. Post-monsoon is a fall season and plant was shading its leaves and some leaves were also yellowish. So, plant preferred to store energy over carbon conversion to isoprene. Thus, monsoon season is the vegetative period. CO_2 assimilation flux was obtained by equation (*Sinha et al 2007*):

$$\mathbf{EF_{CO2}}\ (\mu g\, g^{-1}\, hr^{-1}) = \frac{\mathbf{m_{in,co2}} - \mathbf{m_{out,co2}}\ (\mathrm{nmol\ mol^{-1}})}{\mathbf{V_m}(m^3\ mol^{-1})} \times \frac{\mathbf{M.W.}\,(g\ mol^{-1}) \times \mathbf{Q}\ (m^3\ hr^{-1})}{\mathbf{W}\ (g)}$$

where,

- **Q** is the flow rate of the input air into the plant chamber ($m^3 s^{-1}$)
- **W** is the dry weight of the leaves enclosed by the plant chamber in gm
- $\mathbf{m}_{in,co2}$ is the mixing ratio VOC in the inflowing scrubbed air (nmol mol^{-1})
- $\mathbf{m}_{out,co2}$ is the mixing ratio of VOC in the outflowing air from the plant chamber (nmol mol^{-1})
- $\mathbf{M}_{co2}$ is the molecular weight of the VOC in kg mol^{-1}
- V_m is the molar gas volume in m^3 mol^{-1}

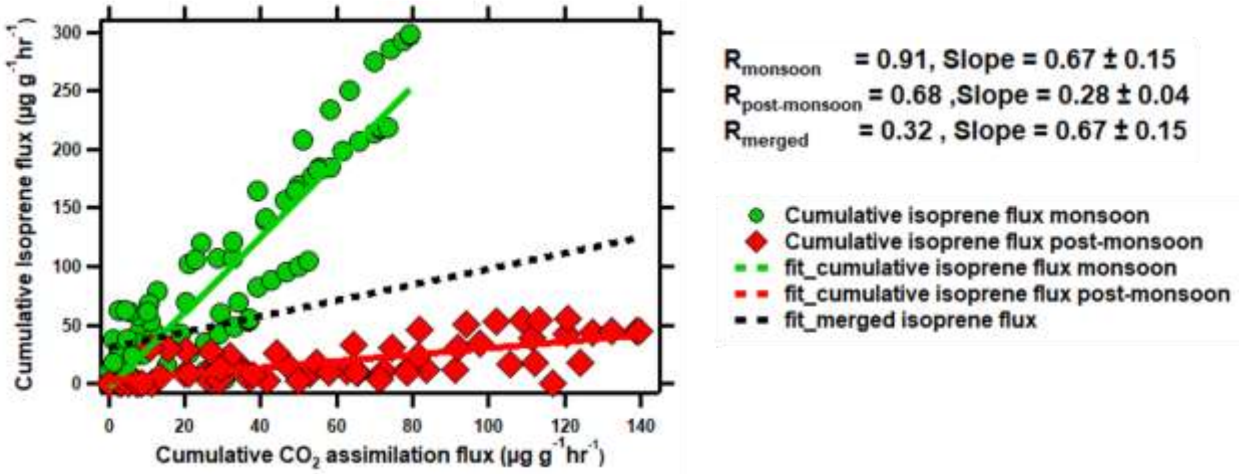


Figure 3 g) Cumulative isoprene flux (PTR-QMS) v/s cumulative CO_2 assimilation flux (CRDS) for both monsoon and post-monsoon seasons.

A time-series was plotted for isoprene mixing ratio obtained with TD-GC-FID and PTR-QMS instruments and is shown in **figure 3 h)** for both the monsoon and post-monsoon seasons. During monsoon maximum isoprene mixing ratio observed was 443.08 ppbv and 416.90 ppbv with TD-GC-FID and PTR-QMS respectively on 08/10/2018, 09:24 hour and during post-monsoon maximum isoprene mixing ratio observed was 34.64 ppbv and 20.36 ppbv with TD-GC-FID and PTR-QMS respectively on 11/30/2018, 10:40 hour. A correlation plot of isoprene mixing ratio with two instruments is shown in **figure 3 i)**. An R value of 0.98 and 0.96 with slope value of 0.96 ± 0.03 and 0.84 ± 0.07 was obtained during monsoon and post-monsoon season. A large difference between isoprene mixing ratio and R value during post-monsoon with two instruments can be explained in the terms of unavailability of data with PTR-QMS and availability of only one data point in 50 minutes with TD-GC-FID instrument.

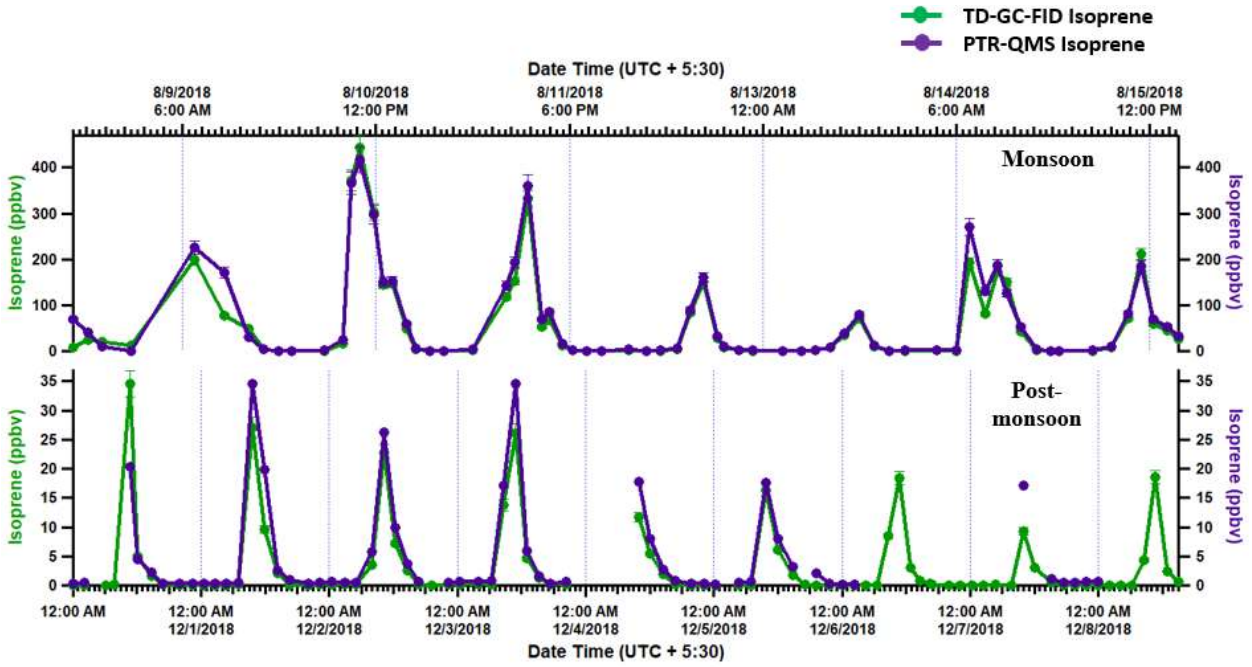


Figure 3 h) Isoprene mixing ratio time series of PTR-QMS and TD-GC-FID instruments.

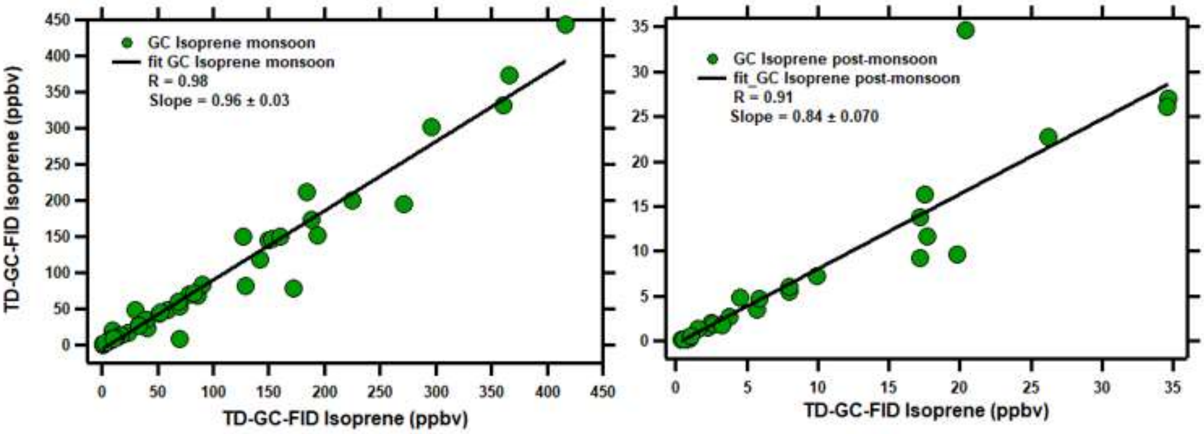


Figure 3 i) Correlation between TD-GC-FID and PTR-QMS isoprene mixing ratio.

Chapter 4

Summary and Conclusion

Populus deltoides is an exotic species to India and is widely grown in North India for the agroforestry purpose. This species is useful in cleaning soil and water contaminated with boron and cadmium (*Ball et al. 2005*). On looking thoroughly at the fragmentation pattern obtained for BVOCs with PTR-QMS and chromatograms obtained from TD-GC-FID it was found that *Populus deltoides* emits isoprene as a major BVOC and monoterpenes 81 and 137 in trace amounts. Plant species are categorized into four categories on the basis of their isoprene emission capacity. Negligible Isoprene Emitters, <1 μg $g^{-1}h^{-1}$ e.g. *Moringa oleifera* (Drumstick Tree), Low Isoprene Emitters, 1 to ≤ 10 μg $g^{-1}h^{-1}$ e.g. *Punica granatum* (Pomegranate), Moderate Isoprene Emitter 10 to ≤ 25 μg $g^{-1}h^{-1}$ e.g. *Morus alba* (White Mulberry) and High Isoprene Emitters, ≥ 25 μg $g^{-1}h^{-1}$ e.g. Psidium guajaya (Common guava), (*Singh et al., 2008*). Maximum isoprene flux of *Populus deltoides* during monsoon and post-monsoon season are 67.79 μg $g^{-1}h^{-1}$ and 18.02 μg $g^{-1}h^{-1}$ respectively. *Populus deltoides* is a deciduous species and post-monsoon is the fall season and during this period P*opulus deltoides* started to shade the leaves and some leaves are yellowish and green and during monsoon the plant was full of green leaves. Spring season in India starts during February and March months. Thus, during post-monsoon leaves were at dying stage while during monsoon they are at the mature stage. Thus, it’s a good idea to consider monsoon isoprene flux for *Populus deltoides* to put it into one of the categories for its isoprene emission capacity. During monsoon season maximum isoprene flux obtained was 67.79 μg $g^{-1}h^{-1}$ thus *Populus deltoides* falls in the category of **high isoprene emitters**. Average isoprene flux during monsoon and post-monsoon are 13.66 μg $g^{-1}h^{-1}$ and 4.51 μg $g^{-1}h^{-1}$ in terms of leaf der weight and 2.31 nmol m^{-2} s^{-1} and 1.51 nmol m^{-2} s^{-1} in terms of leaf area respectively. In India both monsoon and post-monsoon period have a duration of four months thus total isoprene flux over India due to *Populus deltoides* during both monsoon and post-monsoon seasons are 5.42 Gg yr^{-1} and 3.55 Gg yr^{-1} respectively .

The obtained maximum isoprene flux value during monsoon season is comparable to the value sited in the literature, 53.6 μg $g^{-1}hr^{-1}$ normalized at 30°C and 1000 μmol$m^{-2}s^{-1}$ (Singh et al., 2008). On looking at **figure 3 h)** *Populus deltoides* in-takes a large flux of CO_2 during both monsoon and post-monsoon seasons. Thus, it is a good carbon sequestration source from the atmosphere and soil (*Arora et al., 2015*).

To increase the greenery in states and countries plants are planted in a large amount nowadays which includes avenue plantation. *Populus deltoides* is a widely grown plant species because of its high growth rate of 20-25 $m^3ha^{-1}yr^{-1}$ and an out- turn of 5.05 million tonne/yr fresh wood (Country report 2012-2015). This plant species is a high isoprene emitter and this isoprene is a competitor to CO and CH_4 in the atmosphere as discussed in Chapter 1 introduction. So, during planting this species all these factors should be considered. The obtained isoprene flux value can be used in models to get global isoprene flux value due to *Populus deltoides.*

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