Parametrization of the DO3SE model and analysis of stomatal flux measurements for different tree species

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Certificate of Examination

This is to certify that the dissertation titled " Parametrization of the DO3SE model and analysis of stomatal flux measurements for different tree species " submitted by Mr. Ebin George (Reg. No. MS12101) 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.

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(Supervisor)

Dated: April 21, 2017

Declaration

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

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Dated: April 21, 2017

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. Bärbel Sinha

(Supervisor)

Acknowledgement

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I would like to also acknowledge the Library of IISER Mohali and its staff for the facilities and services provided.

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Abstract

Troposheric ozone is a major pollutant that acts as a greenhouse gas and is harmful to humans as well as plants. The toxic effect of ozone to plants include yield loss, leaf injury etc.. Different ozone exposure metrices like Mx, W126, AOT40 were used in the past to determine a O_3dose/plant response relationship. In this study, we are looking at a new metric known as PODy (phytotoxic Ozone Dose). This metric was developed based on the stomatal flux measurements as a measure of ozone that enters the stomata of a leaf. Ozone was measured using UV absorption photometry and the stomatal conductance measurements were done using a leaf porometer. Proper calibrations were performed for both instruments for data quality and assurance. Stomatal conductance measurements were taken on the leaves of 5 different tree species namely, Arjun, False Ashoka, Jamun, Neem and Peepal around the campus during the December 2016- February 2017. These trees are most abundantly found in the cities of India. Stomatal conductance values along with the temperature, pressure, humidity, solar radiation, ambient O_3 measurements were in cooperated into the DO3SE (Deposition of Ozone for Stomatal Exchange Model). The DO3SE model was calibrated by boundary line parameterization for parameters like temperature, vapor pressure deficit and solar radiation in a species-specific manner. The modelled v/s measured comparison was done for the stomatal conductance values and best correlations were observed for False Ashoka, Jamun and Neem. There are nearly 17,000 False Ashoka trees present in Chandigrah. POD_0 value for False Ashoka is calculated to be 7.7 mmol m^{-2} and the total ozone uptake by all False Ashoka trees in Chandigrah assuming a crown diameter of 2 m and a leaf area index (LAI) of 4 is about 26.5 kg of ozone during the month of January alone. In the urban atmosphere, trees can play a major role in the removal of pollutants and help in maintaining the ozone levels under control by dry deposition process. Similarly, NO_2 intake can also

be calculated with the help of diffusivity ratio between NO_2 and O_3(1.01). The NO_2y value is 8.16 and the total removal is 26.9 kg of NO_2.

Chapter 1

Introduction

1.1 Troposheric ozone chemistry

Ozone is a gas with the formula O_3, which acts as aggressive oxidizing agent. When present in the troposphere it is an air pollutant which negatively affects human health [30], crop yields [29] and natural ecosystems [31], primarily by causing reactive oxygen stress [5]. In India ozone exposure is regulated by the National Ambient Air Quality Standard, which prescribes ozone primary and secondary levels to be 100 ug/m^3 (8 hr) and 180 ug/m^3 (1 hr) respectively i.e, approximately equal to 50 ppb (8 hr) and 90 ppb (1 hr) at NTP [40].
In Mohali, the 8hr threshold considered safe for humans is exceeded 62% of the time throughout the year [28]. Exceedance events occur throughout the year except on overcast or foggy days. The safe threshold for vegetation of 40 ppb [29] is exceeded much more frequently and 10,000 -16,000 ppbh of AOT 40 are accumulated during the wheat growing season. In this thesis I use stromatal flux measurements to quantify what ecosystem services trees deliver through their stomatal ozone uptake and assess the risk of ozone damage to trees.

In 1950s, Blacet showed that there is production of troposheric ozone by photolysis of NO_2 in polluted areas. The reactions involved in the photochemical NO_x cycle are:

$$\mathrm{NO_2 + hv(\lambda \leq 420nm)} \xrightarrow[\mathrm{cm^3molecule^{-1}s^{-1}}]{\mathrm{k_{(298)} = 3.0E^{-14}}} \mathrm{NO + O(^3P)} \qquad \text{(R1)}$$

$$O(^3P) + O_2 + M \xrightarrow[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]{k_{(298)} = 6.1E^{-34}} NO_2 + O_2 \qquad (R2)$$

$$NO + O_3 \xrightarrow[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]{k_{(298)} = 1.9E^{-14}} NO_2 + O_2 \qquad (R3)$$

But,this is again a null cycle.Therefore, there must be other reactions involved for the production of ozone. Now we have to consider the role of VOCs and the HO_x chemistry. A very few part(less than 1%) of excited state of O radical contribute to the formation of OH radical.RO_2 and HO_2 are formed by the initiation reaction of OH radical.

$$RH + OH \xrightarrow[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]{k_{(298)} = (0.1 - 7)E^{-12}} R + H_2O \qquad (R4)$$

$$R + O_2 + M \xrightarrow[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]{k_{(298)} = (0.2 - 8)E^{-11}} RO_2 + M \qquad (R5)$$

Reaction of alkyl peroxy radical with NO is the most significant and leads to the formation of NO_2.

$$RO_2 + NO \xrightarrow[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]{k_{(298)} = (7.5 - 9)E^{-12}} RO + NO_2 \qquad (R6)$$

$$RO + O_2 \xrightarrow[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]{k_{(298)} = 4E^{-12}} RCHO + HO_2 \qquad (R7)$$

$$HO_2 + NO \xrightarrow[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]{k_{(298)} = 8E^{-12}} NO_2 + OH \qquad (R8)$$

Then, the photochemical NO_x cycle(R1 - R3) participates for the production of O_3. Finally,the chain is broken by either of these two reactions:

$$HO_2 + HO_2 \xrightarrow[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]{k_{(298)} = 1.7E^{-12}} H_2O_2 + O_2 \qquad (R9)$$

$$NO_2 + OH + M \xrightarrow[\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]{k_{(298)} = 2.2E^{-30}} HNO_3 + M \qquad (R10)$$

In a NO_x limited regime,reaction R9 has a high rate compared to reaction R10 and ozone production rate rate has a liner dependence on [NO]. H_2O_2 is a reservoir for OH and HO_2. Whereas, in the VOC limited regime, rate of reaction R10 is higher with an inverse dependence on [NO_2] and linear dependence on [RH].

$$P_{O_3} = 2k_{HO_2+NO}(\frac{P_{HO_x}}{2k_{HO_2+HO_2}})^{1/2}[NO] \tag{1.1}$$

$$P_{O_3} = \frac{k_{RH+OH}P_{HO_x}[RH]}{k_{OH+NO_2}[NO_2][M]} \tag{1.2}$$

All the reactions and rate constants were taken from the book "Chemistry of Upper and Lower Atmosphere by Barbara J. Finlayson-Pitts and James N.Pitts,Jr".

Troposheric Ozone budget

Ozone is a very important greenhouse gas. We can see that the major source and sink contribution is through the chemical processes. The sources and sinks of ozone are given in the pie charts given below

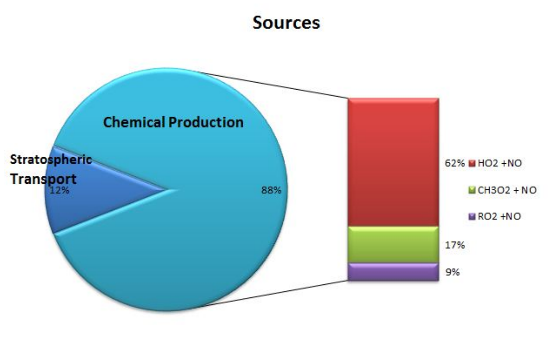

Figure 1.1: Troposheric Ozone sources

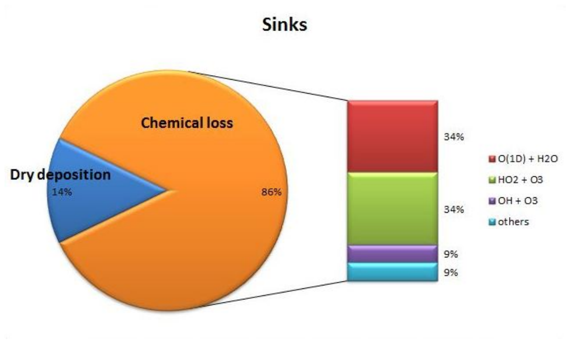

Figure 1.2: Troposheric Ozone sinks

Sources and sinks constitute about 3400-5700 Tg O_3 yr^{-1}. This data is from the book "Introduction to Atmospheric Chemistry by Daniel Jacobs".

1.2 Ozone pollution and its effects on plants

Current ozone concentrations are higher in the Northern hemisphere than in the Southern hemisphere[32]. The highest concentration of ozone occur during summers with a peak daily concentration attained during afternoon[28]. Ozone can induce oxidative stress in living organisms and it is considered as an important phytotoxic air pollutant affecting vegetation. It was also observed that prolonged exposure to ozone can affect isoprene emissions in *P.alba* leaves[14]. Exposure to high levels of ozone reduced net photosynthesis which in turn were related to decline in growth and yield of crops[3]. Elevated O_3 has also weakened the sink strength of carbon in the soil-tree system and can also cause reduction in the stem growth[4]. Many studies have shown that chronic ozone can reduce the stomatal conductance affecting the reproductive growth of the plant. Ozone is also reported to have caused damage to forests[33].

Plants can withstand a certain level of ozone pollution through detoxification process. But, when the concentration exceeds a certain level, ozone impairs plant metabolism leading to yield reduction in agricultural crops. Ozone enters the plants through stomata which is also a site for CO_2 entry. O_3 entering inside the apoplast reacts rapidly with molecules that can cause production of other ROS,including hydrogen peroxide,superoxide radicals,hydroxyl radicals. The quenching capacity of ROS in the apoplast through reactions with antioxidants marks the first line of defence against O_3 damage. At high levels, ROS can cause programmed cell death.It has also been established that plant growth in chronic O_3 is characterized by decreased rates of CO_2 assimilation at leaf level.In addition to the decreased CO_2, plants are also impacted by indirected costs associated with detoxification needed to counter the ROS increase generated by O_3.

1.3 Historical evolution of ozone exposure metrices

The phytotoxic effects of ozone include yield loss, leaf injury, reduction in reproductive growth etc.. Research indicates that O_3 alone was responsible for 90% crop loss caused by air pollution[19]. Studies were conducted in US and Europe to learn about ozone exposure plant response relationships. There are 3 main factors for exposure-response based system, 1)a measure to understand the response of a plant which in most cases is crop yield, 2)an exposure metric which can be used as an index for ozone dose that impacted the plant, 3)a model that links this response exposure system. The major contributions in this field were primarily by the US and Europe. In 1979,US EPA recognized the importance of a separate standard for the effects of ozone on ecosystem. In 1980, through NCLAN(National Crop Loss Assessment Network),the first major study on the impacts of ozone on crops was done. During the program,the crops were grown in Open Top Chambers(OTC) in which plants were exposed to fixed levels of ozone and they were monitored during the crop growing season. At the beginning, ex-situ ozone was added in excess of ambient for 7h/day which was later changed to 12h/day. This was the beginning of the first ozone exposure metric known as the M_x metric.[20]

$$M_x = \frac{1}{n}\sum_{i=1}[C(O_3)]_i \tag{1.3}$$

M_x metric is defined as the mean daytime 7h (M7) and 12h (M12) surface ozone concentrations during the daylight hours 09:00-15:59 and 08:00-19:59 respectively in the crop growing season. It was observed that spikes of peak concentrations of O_3 affected the plants more than a long exposure to low O_3 concentration. It was also understood that the the effects are cumulative[7]. Based on this new exposure metric giving more weightage to higher levels of O_3 were developed by Rawlings et al.(1988) and Lee et al.(1988)[21], [22]. But, the more widely accepted was the W126 metric developed by Lefon et al.(1988)[23]

$$W126 = \sum_{i=1}^{n}[\frac{C(O_3)}{1 + 4403 \exp -0.126C(O_3)}] \tag{1.4}$$

WI26 metric is defined as the weighted sum of hourly ozone concentrations during daylight hours during the crop growing season. The weight used is a sigmoid function.This metric gives more weightage to higher concentration and still includes lower concentration[24]. In the context of Europe,the concept of critical levels were used.That is, only cumulative exposure over a certain critical level is considered. Based on the EOTC(European Open Top Chamber)experiments,it was found that crops were affected above a threshold of 40 ppb. Later UN/ECE ICP–Vegetation Program (United Nations Economic Commission for Europe International Cooperative Program on effects of air pollution and other stresses on crops and non wood plants) accepted a new metric known as the AOT40 metric[25].

$$AOT40 = \int max(O3 - 40ppb, 0.0)dt \tag{1.5}$$

AOT 40 is defined as the accumulated excess of hourly ozone concentration above 40 ppb (80 ug/m^3) between a time zone of 8:00 and 20:00 in the growing months of a certain cultivar[5]. Integral is taken overtime for a vegetation (growing season) and for daytime only. Its main advantage is that it integrates exposure over time for biological importance and that to over higher concentrations. But, sometimes AOT 40 may not be good enough. For example, in places where ambient is less than 40 ppb, high concentration detection due to small measurement errors or spatial difference in concentration can have a large effect on AOT 40. In this case, the best metric to use is M_x since it take into account all concentrations. Overall, the impacts of ozone are often better related to accumulated exposure above a threshold concentration. LRTAP (Long-Range Transboundary Air Pollution) Convention accepted the critical level AOT40 concept in 1993.

By late 20th century, it was realized that there was no direct correlation of plant damage with ambient ozone concentrations. Dry deposition is an important and recently much debated ozone sink. While Daniel Jacobs in his study on the tropospheric ozone budget reported that it constituted 14% of the sink term, a more recent paper by Fares et al.(2013) suggested that the contribution could be as large as 21% globally and that the dry deposition loss term dominated over the chemical loss term for boundary layer losses. This deposition process is mainly performed by the ecosystem through stomata. It was then acknowledged that only the ozone that enters the plant through the stomata affected the plants[26].

The new metric found on the basis of stomatal flux is phytotoxic ozone dose $(POD)_y$. This metric is developed on the basis of different parameters like temperature, vapor pressure defcit, solar radiation, plant phenology, soil water potential, ambient O_3 concentration and it's effect on O_3 uptake by plants[18]. It is defined as the accumulated stomatal ozone flux over a threshold Y nmol m^{-2} s^{-1}.

$$POD_y = \int max(F_{st} - Y, 0.0)dt \tag{1.6}$$

Where Fst is the stomatal flux and Y is the threshold.

In some drought affected areas, it was observed that even high concentrations of ozone did not cause any plant damage. Further studies proved that ozone injury was eliminated by stomatal closure[17]. Stress conditions from the drought had closed the stomata. This was a case that proved O_3 uptake through stomata or stomatal ozone flux was better than other metrices for learning O_3 related risk assessment.

1.4 DO3SE Model

DO3SE model stands for deposition of ozone for stomatal exchange. DO3SE model was accepted by the EMEP LRTAP Convention in 2007[27]. This model helps in calculating the stomatal flux. Its approach for stomatal resistance is based on a multiplicative stomatal conductance model described by Jarvis(1976) and modified by Korner et al(1995). This has been further developed to get a species specific stomatal conductance.

G_{max} is the species specific maximum stomata conductance to ozone ($mmolm^{-2}s^{-1}$) expressed on a total leaf surface area. All parameters are expressed as the modification of gmax to the above mentioned factors. Phenology function tends to increase slowly through the growing season and then decreases when the growing season ends. gpot gives a value of 1 at the middle of growing season. Only g_{temp} is the same.

$$G_{sto} = g_{max} * g_{pot} * max\{g_{min}, (g_{light} * g_{temp} * g_{VPD} * g_{SWP})\}$$

$$f_{temp} = max\{f_{min}, [(T - T_{min})/(T_{opt} - T_{min})] * [(T_{max} – T)/(T_{max} – T_{opt})]^{bt}\}$$

$$bt = (T_{max} - T_{opt})/(T_{opt} – T_{min})$$

$$f_{VPD} = min\{1, max\{f_{min}, ((1 - f_{min}) * (VPD_{min} - VPD)/(VPD_{min} - VPD_{max})) + f_{min}\}\}$$

$$f_{light} = 1 - exp((-light_a) * PFD)$$

The main use of using this model is to generate results for integrated assessment modeling(IAM). The fact that the calculations of concentration are done close to the canopy so that we can see more prominent effects help to outweigh the uncertainties involved. From, this model we will be able to calculate the PODy (phytotoxic ozone dose) which is now the newly accepted flux based index. The effects are addressed by the relations between the stomatal ozone flux and the meteorological conditions. This helps in the ozone risk assessment. Concentration based indices are easy to use as they are calculable just by the ozone concentrations alone. But, they are inadequate for risk assessment of plants growing in harsh conditions like places with high temperature, drought etc. The flux model incorporates the effects of meteorological conditions[10].

The model stimulates the effect of phenology, irradiance, temperature, vapour pressure deficit on stomatal conductance. In many cases high ozone flux is were modeled in association with only moderate AOT40 values. The factors that cause the limiting of the ozone uptake were VPD, soil moisture deficit, and phenology. The limiting effect of VPD is very clear since, high VPD result in stomatal closure which tends to co-occur with high ozone concentrations. High soil moisture deficits can also result in reduced stomatal conductance[11].

Chapter 2

Materials and Methods

2.1 Site description

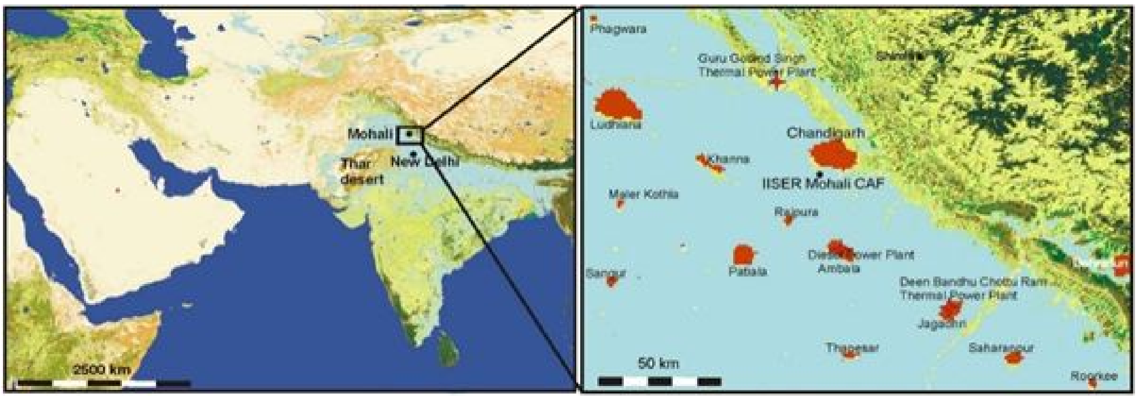

Figure 2.1: Left: Location of Mohali, in the NW-IGP. Right: Map of the land use in a 100 km*200 km area surrounding the measurement site (black dot, 30.667° N, 76.729°E, 310 m asl)

All the measurements were taken inside IISER Mohali(30.667°N - 76.729°E, 310m asl) from the IISER Mohali atmospheric facility and leaf conductance measurements were also taken from trees inside the campus. The city of Mohali is located in the northwest Indo-Gangetic Plain in the Indian state of Punjab as shown in the figure.The nearest neighbouring cities include Mohali,Chandigarh and Panchkula. According to the 2015 report from the Forest Survey of India,Punjab with a geographical area of 50,363 km^2 has a 3.07% of tree cover and Chandigarh with a geographical area of 114 km^2 has a 7.8% tree cover. There has been a decrease in tree cover in Punjab due to rotational fellings and increase in tree cover in chandigarh due to plantation and protection activities.But,the change is minimal. The campus encloses an area of about 1.25 km^2 with more than 1000 residents. Local influences from nearby emissions are significant only at low wind speeds($< 1ms^{-1}$). Normally airmasses arrive at a speed of $(3 - 27ms^{-1})$.

On the basis of direction from the site, different wind sectors are put into different categories. Towards the North to North east of the measurement site comprise of cities like Chandigarh,Mohali and Panchkula known as the urban sector. There are industrial areas which lie in the wind sector from East to South known as Industrial and rural sources. Agricultural activities are predominant in South to North-West direction known as the agricultural and rural sector.

At the measurement site,inlets are located above the Ambient Air Quality Station(AAQS) about 15 m above the ground. These inlets are made of teflon with a diameter of 3.2 mm and length less than 5 m. There are separate inlets for each instrument and large dust particles are filtered for each inlet using Teflon membrane particle filter of 5um pore size. These are changed every week for data quality assurance. The flow rate is measured by BIOS dry definer 220 flow calibrator. Ozone analyzer requires a flow of about 700 sccm which can go to a minimum of 450 sccm.The inlet residence time for Ozone analyzer is less than 6 seconds.

For taking the stomatal conductance measurements ,Leaf porometer was used. It is a portable device.This was also calibrated each day before it's use for data quality assurance.

2.2 Zero Air Generator

The model of Zero Air Generator is Thermo Scientific's Model 1160 Zero Air Supply which converts ambient air to pollutant free air. ZAG consists of different scrubbers and filters to remove the pollutants. For example;

1.Charcoal scrubber removes SO_2,O_3 and hydrocarbons(VOCs).

2.Drierite scrubber removes water.

3.Purafil scrubber removes NO_x.

4.Ascartite scrubber removes CO_2.

There are also many other components like coalescing filters, regenerative dryer,

Membrane dryer and catalytic converter present for removal of the contaminants and pollutants.
Zero Air Generator is required to provide dry purge air for the instruments to perform weekly zero calibrations and monthly span calibrations.

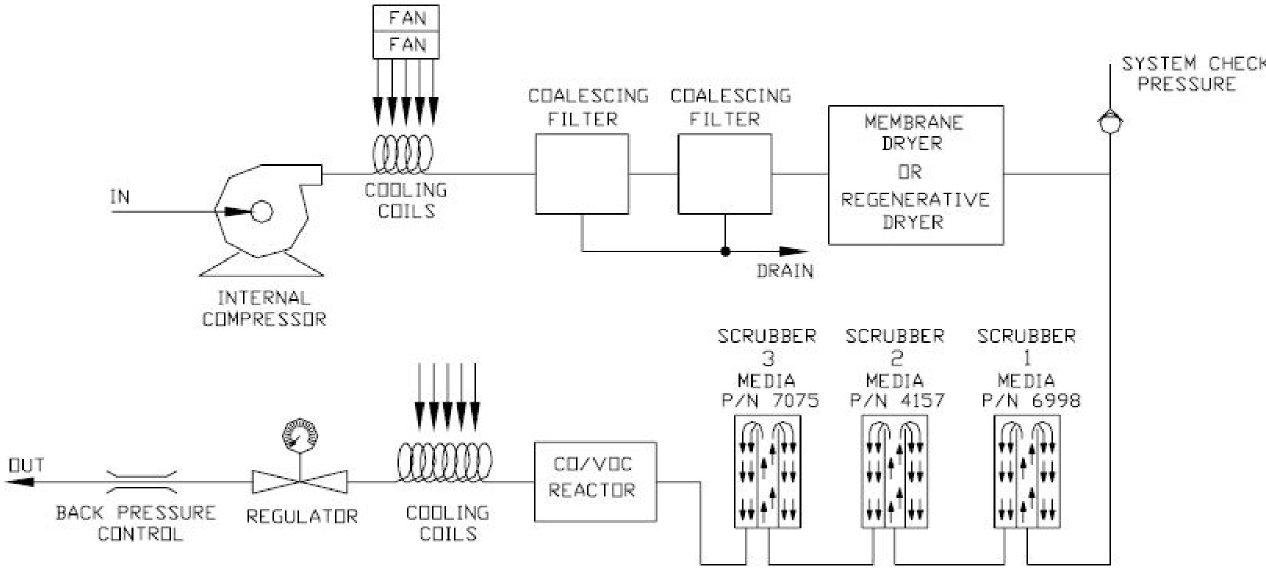

Figure 2.2: Flow diagram of ZAG(This figure is obtained from Thermo Fischer Scientific Model ZAG1160 Instruction Manual,page 1-3)

Ambient air is drawn into the instrument by the internal compressor which provides a flow of about 20 LPM at pressures upto 50 psi. It then enters a loop where air from the fan cools the air stream and water is removed. Membrane dryer or heatless regenerative dryer further dries the air.It is passed through a series of scrubbers to remove a variety of pollutants. It then goes into the converter for removal of CO and VOCs. It then passes through the pressure regulator out into the rear panel.The resultant air coming out of the system is zero air or is a clean diluent air that is used for calibrations which in turn enables data quality assurance.

2.3 Ozone Primary Standard Generator

The Model 49i Primary Standard UV Photometric ozone Calibrator is used for the calculation of zero drift and muti point calibration of ozone analyzer. This instrument can generate ozone in-stiu and along with the zero air from the Zero Air Generator can give desired concentrations of ozone that is required for the calibration.

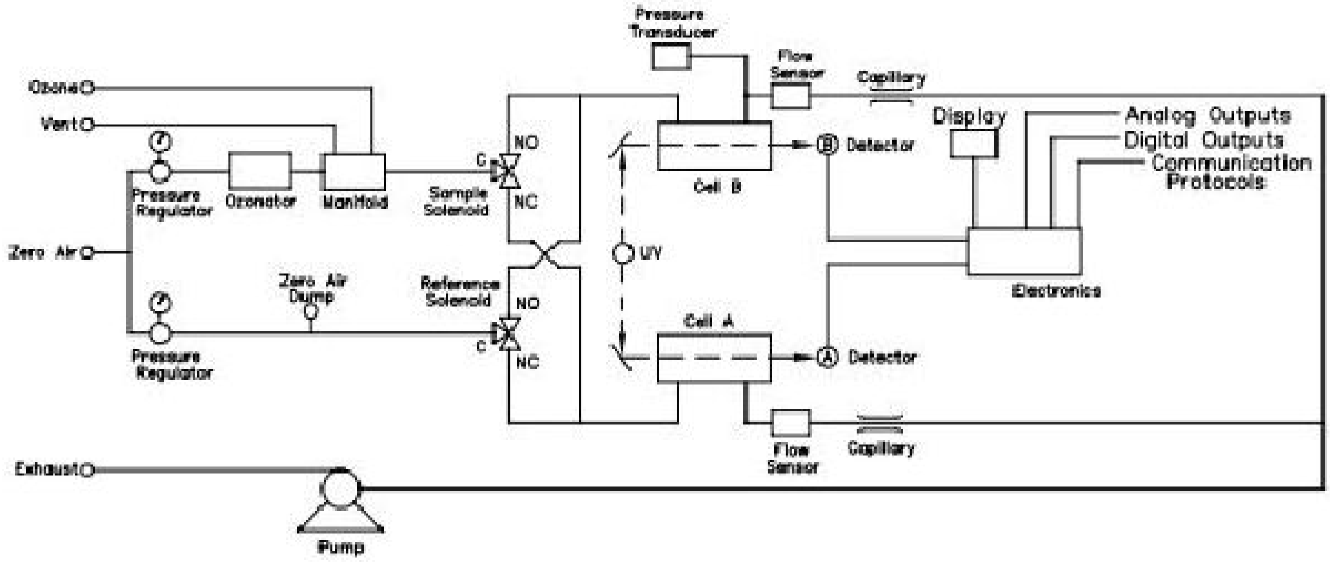

Figure 2.3: Flow schematic of Ozone Primary Standard (This figure is obtained from Thermo Fischer Scientific Model 49i Instruction Manual,page 1-3)

Zero Air from the Zero Air Generator is fed into the zero air bulkhead of Model 49i Primary Generator. The ozone detection is performed by the principle of Beer-Lambert Law. The gas stream passing through the bulkhead is separated into two,one which passes through a pressure regulator to the reference solenoid valve to become the reference gas (I_0). The other passes through the pressure regulator, ozonator and manifold to the sample solenoid valve to become the sample gas(I). In-situ ozone is generated in the ozonator.O_2 mlecule splits into two O atoms and then the O atoms later combine with O_2 molecules to generate o_3. The O_2 molecule absorption maxima of UV radiation is at 185 nm. Then, homogeneous mixture of ozone and zero air happens in the mixing chamber. The sample gas will now consists of sample with ozone and the reference line consists of sample without ozone. Hg lamp is used as a constant source of UV radiation of a wavelength of 253.65 nm. The photo detectors are used for measuring the light intensities. UV photometer lamp illuminate both the cell in optical bench containing sample and reference gas with regular switching in interval of 10 sec in each cell.

2.4 Ozone Measurements

The Model 49i UV Photometric Ozone Analyzer is used for the measurement of ambient concentration of ozone.

2.4.1 Principle and Working

Ozone detection and measurement works on the principle that O_3 molecules absorb UV light at a wavelength of 254 nm,which corresponds to an electronic transition from the ground state$^1A_1$ to the excited state $^1B_2$[9].

$$O_3 + hv \longrightarrow O_2 + O \qquad (\lambda < 320nm) \tag{2.1}$$

The ozone molecules thus absorb the UV radiation and use the photometry to measurethe reduction of quanta of light reaching the detector at 254 nm. The degree of reduction depends on the concentration of ozone in the sample cell,pathlength of the sample cell, and the wavelength of the UV light. This is basically given by the formula based on the principle of Beer-Lambert Law. It is given as follows;

$$\frac{I}{I_0} = e^{-KLC} \tag{2.2}$$

where I=UV light intensity of sample gas

I_0 = UV light intensity of reference gas

K = molecular absorption coefficient of ozone, 308 cm^{-1}(at 0°C and 1atm)

L = length of cell, 38 cm

C = Concentration of ozone in sample air

Ambient air is sucked in through the sample inlet and it is then split into 2 streams. One stream pass through the sample solenoid to become sample gas(I) and the other is passed through a ozone scrubber to become the reference gas(I_0). The scrubber is MnO_2 based and consists of a heated wool. Hg lamp is used as a stable source of UV light which emits strongly at wavelength 253.65 nm. UV photometer lamp illuminates both the cell in optical bench containing sample and reference gas with regular switching in interval of 10 sec in each cell. Just after the switching, few seconds data are ignored to ensure proper flushing. Each cell is connected with individual photo-detector diode to measure the light intensities.

2.4.2 Calibration of Ozone Analyzer

The zero calibration is performed every week and span calibration is performed every month for the ozone analyzer for data quality assurance.

The dry purge air for the zero drift check is generated by the Zero Air Generator.The zero air is passed through O_3 primary standard generator(PSG). Only after atleast 30 minutes of stable response, the zero drift is set. External O_3 is traceable to NIST(National Institute of Standards and Technology).

Span calibration or multipoint calibration is performed once in a week. Procedure is the same as that of zero drift check. The ozone is generated in-situ O_3 PS and is then diluted with the zero air from ZAG to give out desired concentrations of ozone. The calibration points used are at 25, 50, 75, 100 and 125 ppb. A calibration curve is plotted between the measured values and introduced values of ozone.The calibration coefficient of ozone analyzer is set by determining the slope of this graph.

Limit of detection of ozone analyzer is defined as 2σ of the stable measured values observed while sampling ozone free air. Total uncertainty of ozone analyzer is calculated as the root mean square propagation of precision and accuracy error. Precision error(PE) is defined as 2σ uncertainty at each dilution point. The accuracy error (AE) is defined as an inherent 1 % uncertainty of external O_3 PSG and 2 % for each Mass flow controller.

$$\text{Total uncertainity} = \sqrt{(\text{precision error})^2 + (\text{accuracy error})^2} \tag{2.3}$$

An example of the span calibration perfomrd is given above.The limit of detection was observed at 0.104 ppb.The one minute data has 5.19%(4.24%(PE);3%(AE)) uncertainty at 25 ppbV and 3.03%(0.49%(PE);3%(AE)) uncertainty at 125 ppbV.The uncertainty is inversly proportional to the ozone concentration.

2.5 Leaf Porometer

The Decagon Devices Leaf Porometer is used for measuring stomatal conductance in leaves.

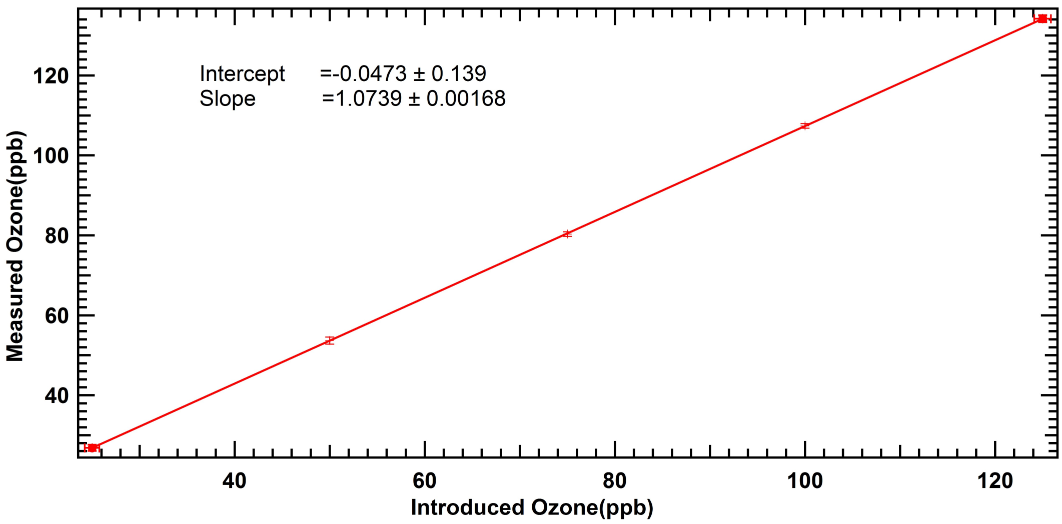

Figure 2.4: O_3 calibration plot of Measured O_3(nmol mol^{-1} Vs Introduced O_3(nmol mol^{-1} on 30-08-2016.

2.5.1 Principle and working

Stomatal conductance is defined as the measure of the rate of passage of carbon dioxide(CO_2) or water vapor through the stomata of a leaf.Stomatal conductance is a function of density, size and degree of opening of stomata, which are pores in plants that open to the outside air.

Leaf porometer measures the stomatal conductance of leaves by putting the conductance of leaf in series with 2 known conductance elements. Water vapor flux can be calculated by measuring the humidity difference across one of the known conductance elements.

The humidity at 3 points is measured i.e at inside the leaf, and at both humidity sensors. Leaf porometer measures the resistance between the leaf and 1st sensor and the 1st and 2nd sensor.

Vapor flux along diffusion path between nodes 1 and 2.

$$F_{vapor} = g_{d2}(C_1 - C_2) \tag{2.4}$$

$$C_i = \frac{h_r e_s(T_a)}{P_{atm}} \tag{2.5}$$

where h_r is the relative humidity, $e_s(T_a)$ is the saturated vapor pressure at air temperature and P_{atm} is the atmospheric pressure. Now, g_d2 is given by the formula,

$$g_{d2} = \frac{\rho D_{vapor}}{d_2} \tag{2.6}$$

where ρ is the molar density of air and D_{vapor} is the diffusivity of water vapor.

$$\rho = 446 \frac{P_a}{101.3}\left(\frac{273.15}{T}\right) \tag{2.7}$$

$$D_{vapor}(T, P_a) = 2.12x10^{-5}\left(\frac{101.3}{P_a}\right)\left(\frac{T}{273.15}\right)^{1.75} \tag{2.8}$$

The final equation becomes:

$$F_{vapor} = \left[\frac{\rho D_{vapo}}{d_2}\right]\frac{1}{P_{atm}}[h_{r1}e_s(T_{a1}) - h_{r1}e_s(T_{a2})] \tag{2.9}$$

1st assumption: The relative humidity within the leaf tissue is 1.0

$$C_{leaf} = \frac{e_s(T_a)}{P_{atm}} \tag{2.10}$$

2nd assumption:All conductive values are in series so that the flux is constant between 2 nodes.

3rd assumption:Temperature of the leaf is equal to the temperature of the first humidity sensor.Therefore, the first equation can be rewritten as equation for node 1 and the leaf node.

$$F_{vapor} = g_{s+d1}(C_{leaf} - C_1) \tag{2.11}$$

Solving it for series combination of conductance i.e,

$$\frac{1}{g_s + d_1} = \frac{1}{g_s} + \frac{1}{d_1} \tag{2.12}$$

we finally obtain the equation for stomatal conductance

$$g_s = \frac{\rho D_{vapor}[h_{r1}e_s(T_{a1} - h_{r2}e_s(T_{a2})]}{[e_s(T_{a1})(1 - h_{r1})]d_2 - [h_{r1}e_s(T_{a1}) - h_{r2}e_s(T_{a2})]d_1} \tag{2.13}$$

In the leaf porometer, the distances are:

d_1 = 3.35mm , d_2 = 11.43mm

2.5.2 Calibration of Leaf Porometer

For taking accurate measurements of stomatal conductance,the teo humidity sensors must behave in a tandem. Over the years, the sensors can change their characteristics, for example, increase in response.Data quality is confirmed by proper and frequent calibration of leaf porometer.

Leaf porometer is calibrated every day it is being used.The calibration of the instrument involves the following steps :

1. The porometer sensor head must be in thermal equilibrium with the environment where the measurements are taken.Therefoe, the leaf porometer along with the components needed for calibration are kept in the environment for about 10 minutes to attain the equilibrium.

2. The sensors must give similar humidity readings to have accurate stomatal conductance readings. For this to happen,the air in the diffusion path must be well mixed which can be done by shaking of the white fluoropolymer agitation bead. If the sensor readings must be stabilized within 2% of relative humidity of each other.

3. The calibration procedure is further performed using a plastic calibration plate which has a drilled hole in the middle. This is covered by a small circular shaped moist filter paper. This calibration plate gives a known conductance of 240 nmol m^{-2} s^{-1}. This will act as the Introduced calibration point.

4. The calibration number will be automatically set in the leaf porometer if there are 3 consecutive measurements all within 7.5% each other.

5. The calibration check can be done using the same plate, by taking it's measurement after the new calibration is set.

Table 2.1: Calibration checks perfomed

Known Conductance (mmol m^{-2}s^-1	**Cal 1**	**Cal 2**	**Cal 3**	**Cal 4**	**Cal 5**
240	06/02/2017	17/02/2017	18/02/2017	20/02/2017	21/02/2017
	231.2	244.9	223	243.6	249.9

From this list of calibration checks, I estimate the precision error of the instrument as 4.17% and accuracy error as 1%.

Chapter 3

Results

3.1 Arjun

Arjun is an evergreen treee and the scientific name of Arjun is *Terminalia arjuna*. This tree has various uses in Ayurveda. It has variety of uses in the medical field especially on heart diseases. There were a total of 85 measurements done on various

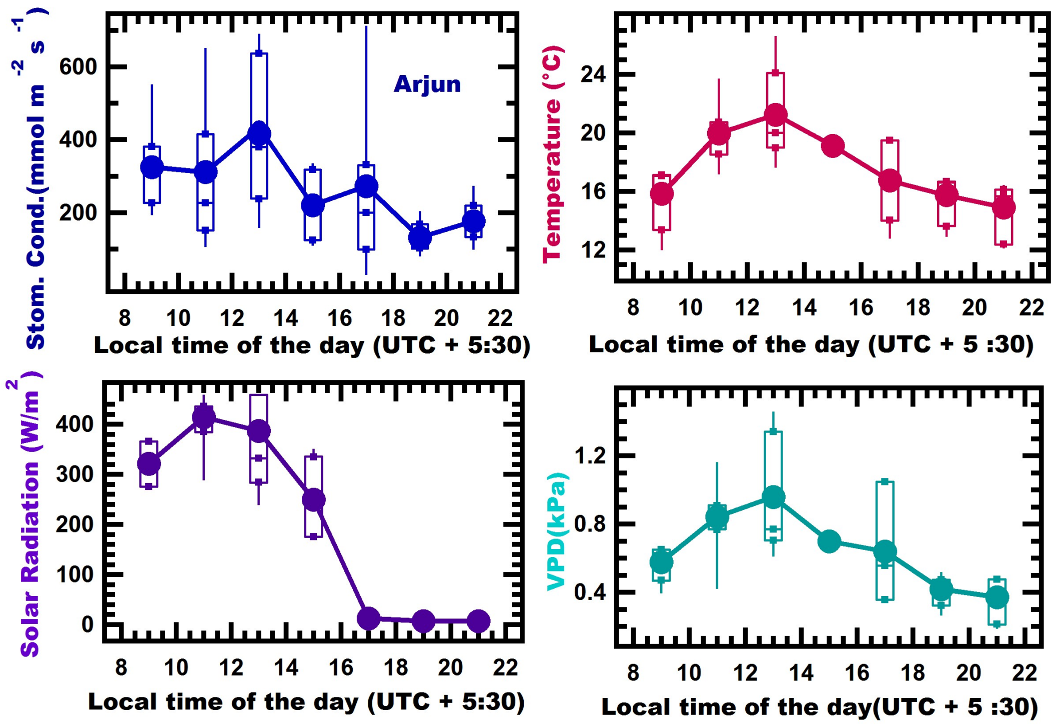

Figure 3.1: Stomatal Conductance of Arjun and Other Parameters

leaves of the plant for this species. From the figure, we can see that the stomatal conductance of Arjun shows a variable trend. It has an average conductance of 350-400 mmol$m^{-2}s^{-1}$ during the daytime till noon. After noon, the conductance keeps on fluctuating but the night time averages lower to 200mmol $m^{-2}s^{-1}$. It is challenging to conclude from this dataset which factors limit conductance. The fact that the stomatal conductance peaks late (at noon) rather than early (before noon) indicates that the trees are not limited by VPD and could point towards the fact that ambient temperatures are below the temperature optimum of the plant which would promote a late conductance maxima. It seems that the respiration rate shortly after sunset (17:00) is almost half of the peak photosynthesis, which is high.

3.2 False Ashoka

False Ashoka is an evergreen treee and the scientific name of False Ashoka is *Polyalthia longifolia*. This tree is a common plant that can be seen in most of the public parks or gardens in India. It is also used for the manufacture of matchsticks, pencils etc.. The number of measurements taken from the leaves of False Ashoka tree are 86. False

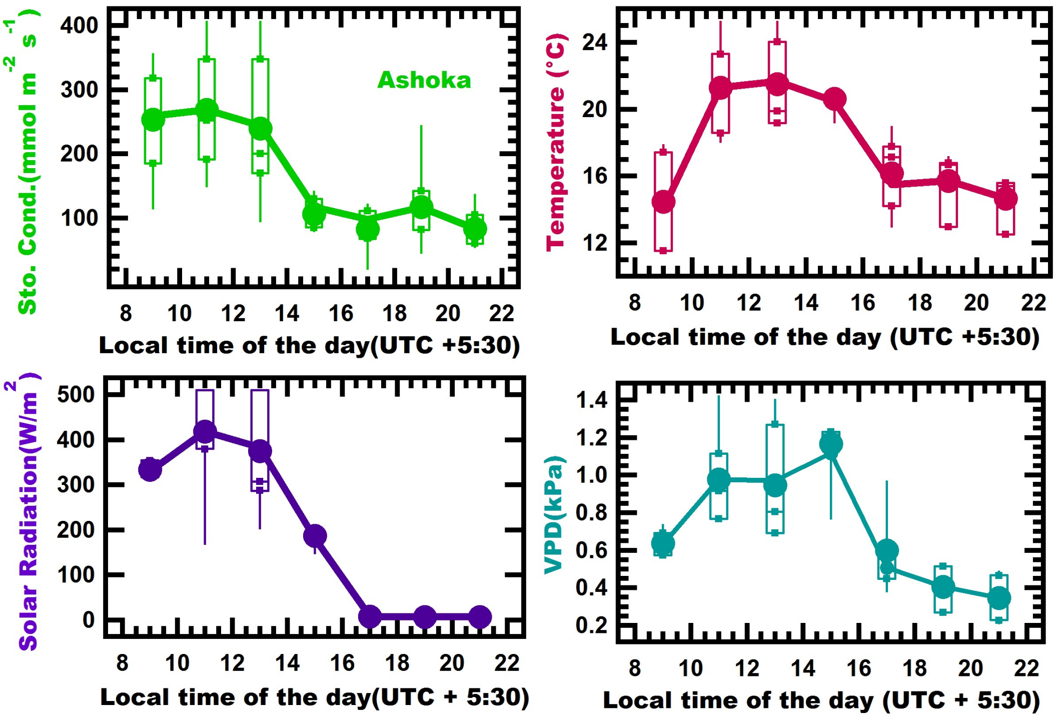

Figure 3.2: Stomatal Conductance of False Ashoka and Other Parameters

Ashoka has an average stomatal conductance of 250 mmol $m^{-2}s^{-1}$ till noon. But, as soon as the vapor pressure deficit increases, the stomatal conductance decreases and remain closed for the rest of the day. The stomatal conductance peaks early (9- 11 am) indicating that the lower early morning temperatures and a slightly suppressed solar radiation (300 W/m^2) are not limiting for the stomatal conductance of this species. A rapid drop can be seen around 3 pm when the VPD suddenly peaks at 1.2 kPa and the solar radiation drops to 200 W/m^2 simultaneously . As a consequence, either of the the two factors could be limiting the stomatal conductance. The respiration rate (average 17:00-21:00) is 95 mmol $m^{-2}s^{-1}$ i.e, about $1/3^{rd}$ of the peak photosynthesis rate.

3.3 Jamun

Jamun is a tropical evergreen tree and the scientific name of Jamun is *Syzygium cumini*. The fruits of Jamun resemble berries and are used for many digestive ailments. The young leaves of jamun are violet in color and finally turn into green as they mature. Total number of measurements taken on jamun is 87. Jamun also

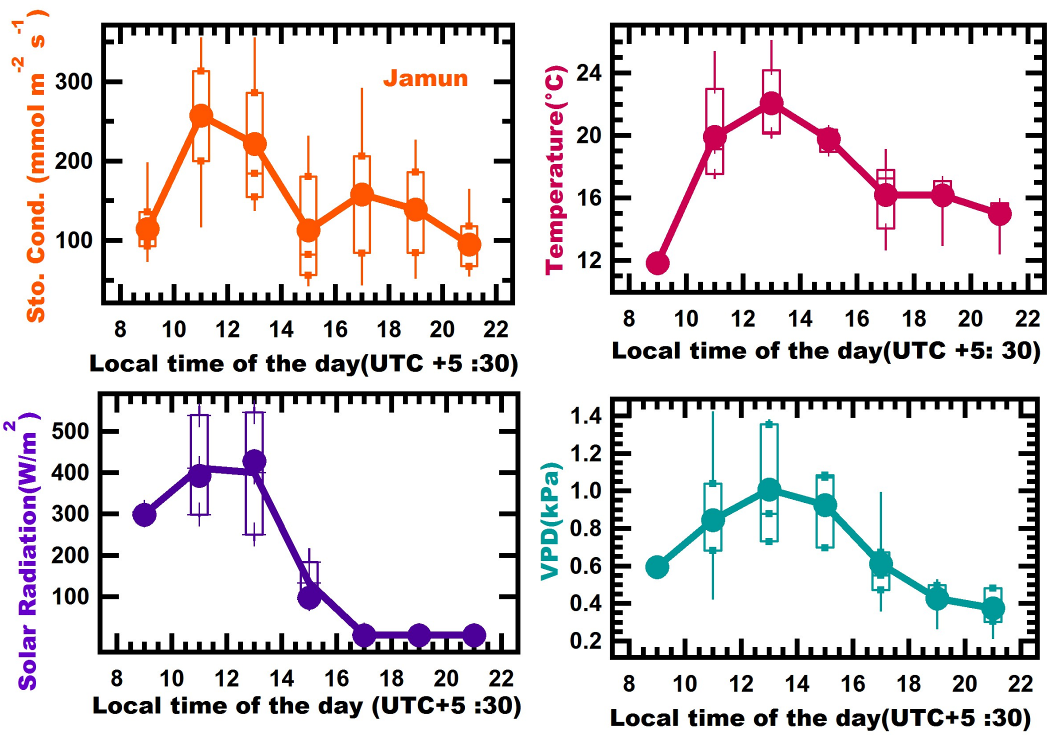

Figure 3.3: Stomatal Conductance of Jamun and Other Parameters

has maximum stomatal conductance during the forenoon time when the maximum photosynthesis occurs. The stomatal conductance dips towards noon (1 pm) despite the fact that the solar radiation is stable and the temperature increases. Since the VPD is increasing in that time window, it could be that the plants are limited by the VPD of water or that the temperatures exceed the optimum temperature of the plant. At 3 pm, there is a sudden dip in stomatal conductance which coincides with a sudden dip of the solar radiation to 100 W/m^2 indicating that solar radiation is the limiting factor here. However the stomata open shortly thereafter for respiration purposes and the peak respiration rate is almost half the peak photosynthesis rate, which is high.

3.4 Neem

Neem is a evergreen treee and the scientific name of Neem is *Azadirachta indica*. Neem is used for a variety of purposes. It is used from toothpastes to constituents for ayurvedic herb. A total of 75 measurements were taken from the leaves of Neem

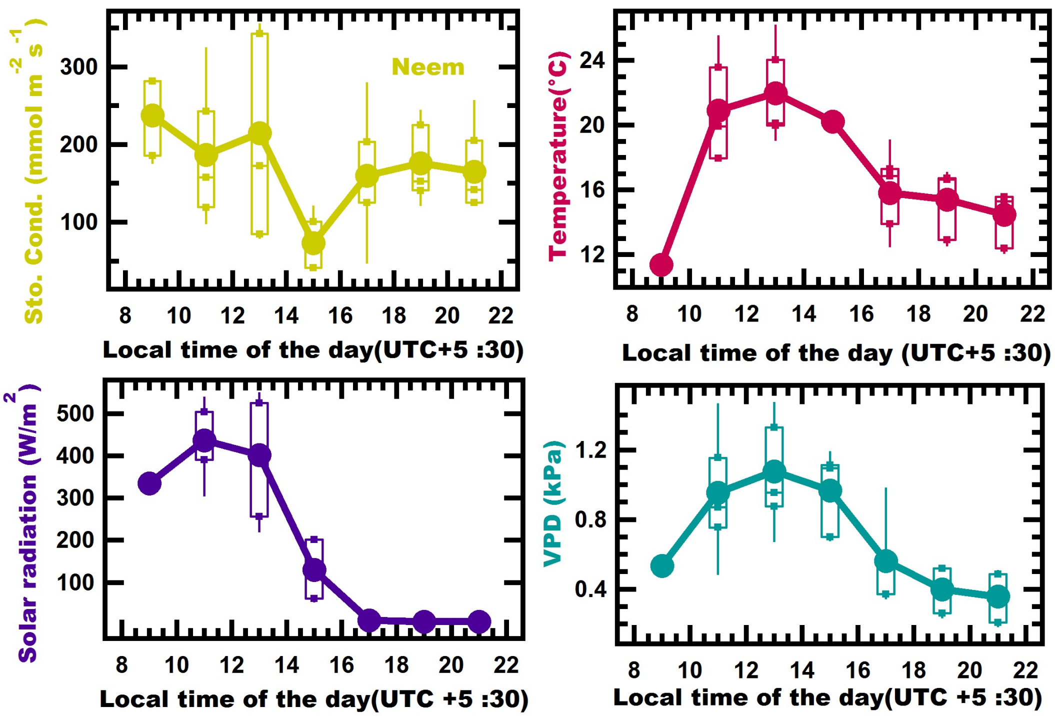

Figure 3.4: Stomatal Conductance of Neem and Other Parameters

tree. Neem maintains an average stomatal conductance within the range of 150 - 250 mmol $m^{-2}s^{-1}$ throughout the day and night except for a small time window between 3-4 pm which can be associated with sudden dip in the solar radiation. No significant result from other parameters show any limiting factor for the conductance. Less number of measurements does not allow us to confirm this trend.

3.5 Peepal

Peepal is a evergreen treee and the scientific name of Peepal is *Ficus religiosa*. Its a traditional medicine as used for variety of cures like diarrhoea, diabetes etc.. 95

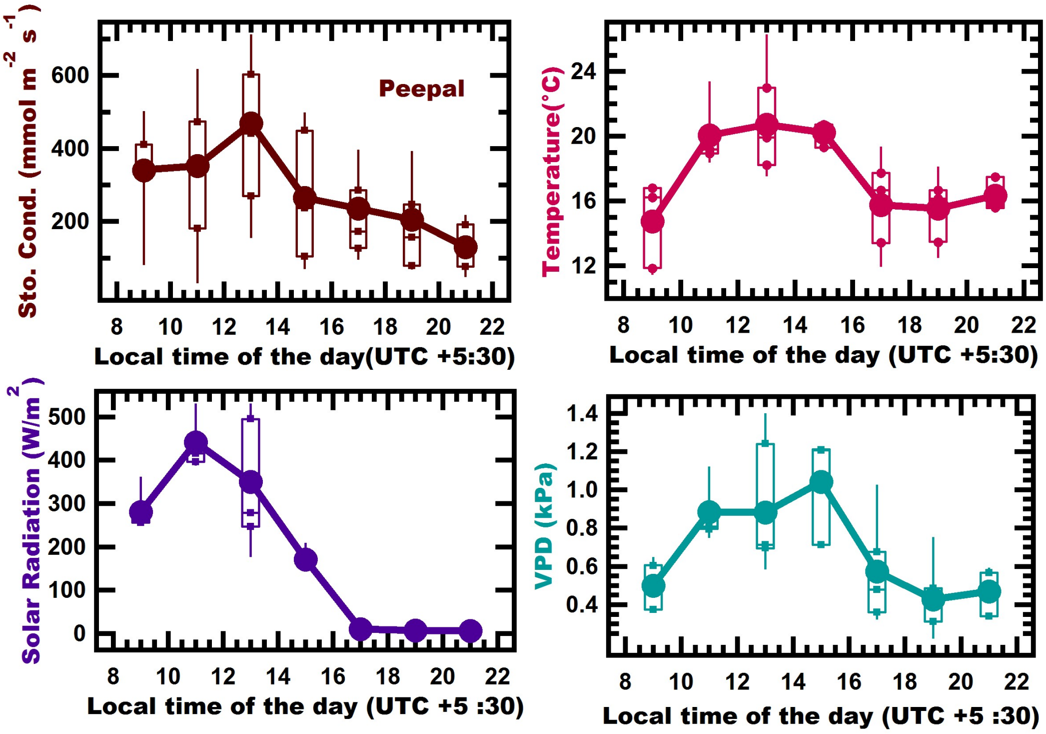

Figure 3.5: Stomatal Conductance of Peepal and Other Parameters

measurements were taken from the leaves of peepal tree. Peepal had the maximum stomatal conductance values close to 400 mmol $m^{-2}s^{-1}$. When the highest values went to 800 mmol $m^{-2}s^{-1}$ during noon, lowest value were observed during midnight less than 100 mmol $m^{-2}s^{-1}$. Again when the vapor pressure deficit values increased,the conductance values decreased but cannot be ascertained that this is the cause for the drop as solar radiation values dip to below 200 W/m^2 simultaneously. However, stomata do remain open throughout the night and the respiration rate is high of about 100-200 mmol $m^{-2}s^{-1}$.

3.6 Parameterization of DO3SE model

All the values of parameters like solar radiation, temperature and vapor pressure deficit were put into the model for each species along with other raw data which includes ambient ozone concentration, pressure as well as humidity data. The boundary line curves were adjusted according to each of the three main parameters and the following values were obtained for each species.

The g_{max} values for each species were the average of the 3 maximum conductance measured from their leaves.

The temperature curve is not complete as there is insufficient data at high temperatures. The temperature curve shows a temperature optimum in which maximum stomatal conductance is observed and for all tree species, it was kept at 25°C. The minimum temperature was 5°C for all species. The maximum temperature was 40°C for Jamun and peepal and 35°C for the rest.

The VPD curve helps to understand a VPD_{min} value after which stomatal conductance values decrease linearly. VPD_{min} can only be identified fro Ashoka, whereas for the others, measurements at lower humidity and higher temperature are required. VPD maximum was 1.4 for all the species except for False Ashoka.

Solar radiation acts a function of a light parameter called $light_a$. But this function does not take into consideration the stomatal conductance values at night time that happen due to respiration which is why there are many points that lie entirely out the boundary lines at low solar radiation.

The soil water potential function was left as it is from the preset values given by the model for evergreen trees.

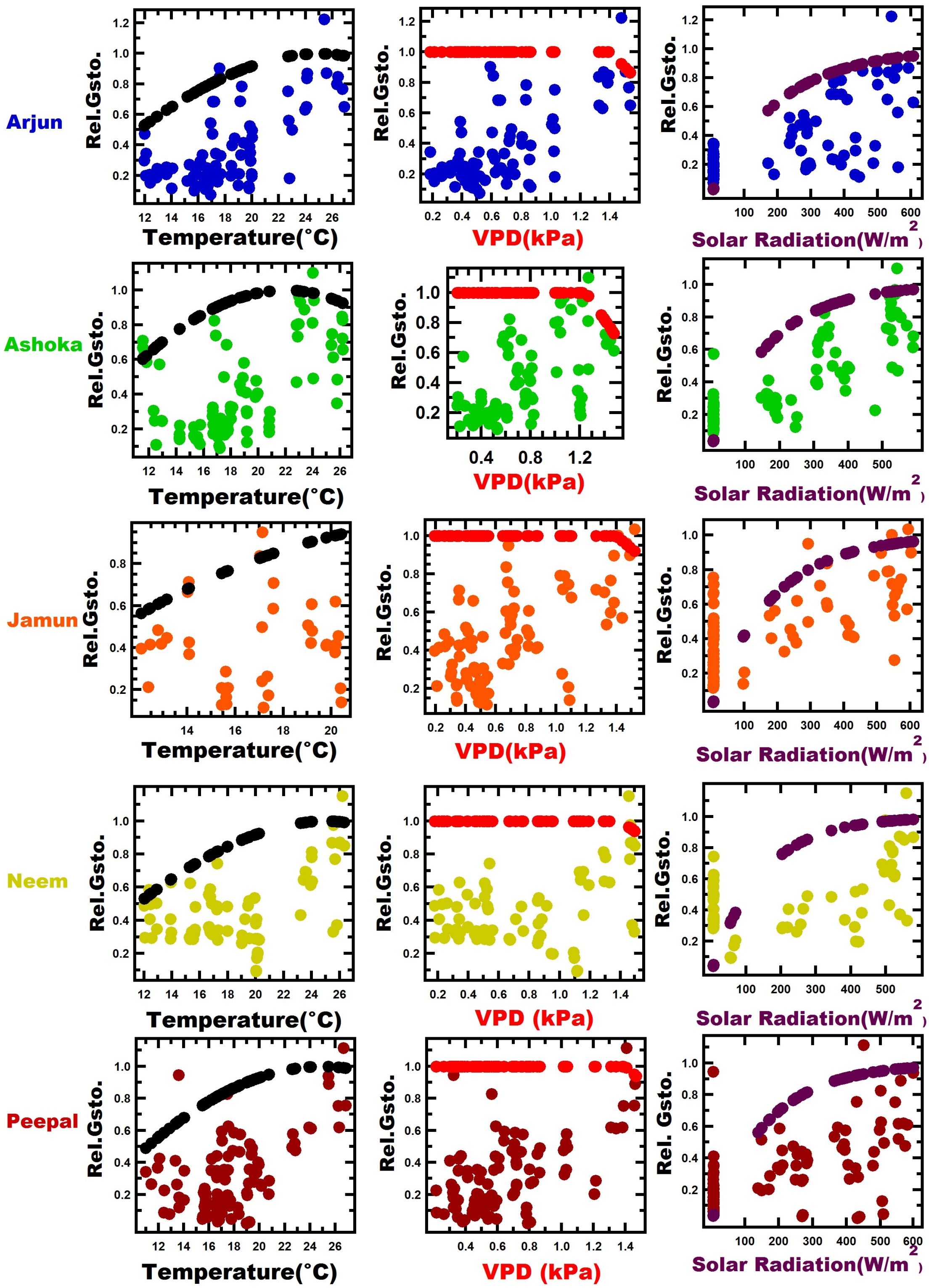

Figure 3.6: Boundary line characterization for the parameters a)temperature b)Vapor pressure deficit and c)solar radiation for different tree species

The stomatal conductance, stomatal ozone flux and PODy values were obtained from the DO3SE model based on these parameterizations.A comparison study was

Table 3.1: Parametrization of model for different trees

Parameters	Arjun	Ashoka	Jamun	Neem	Peepal
g_{max}	803.6	466.1	413.5	421.6	964.8
f_{light}	0.005	0.006	0.005	0.007	0.006
T_{min}	5	5	5	5	5
T_{max}	35	35	40	35	40
T_{opt}	25	25	25	25	22
VPD_{min}	2.4	2	2.9	2.9	2.5
VPD_{max}	1.4	1.25	1.4	1.4	1.4
f_{min}	0.01	0.01	0.01	0.01	0.01

done between the modelled and measured conductance values to find correlations between them.The best fit for all the points ws taken and the intercept was assigned to be 0.

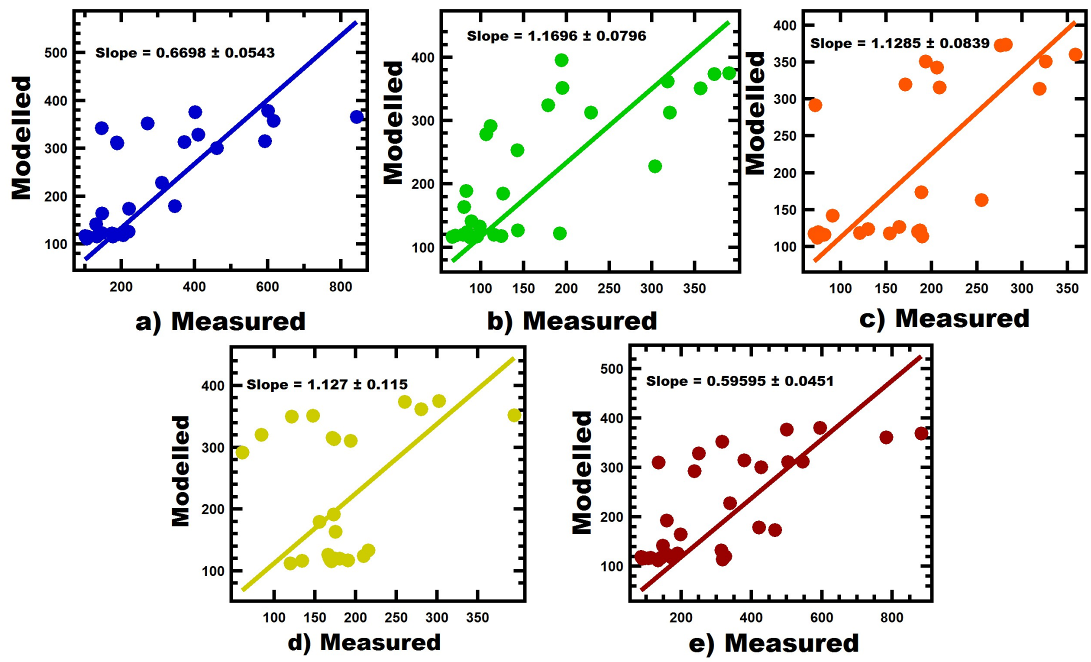

Figure 3.7: Modelled v/s Measured comparison for a)Arjun b)False ashoka c)Jmaun d)Neem e)Peepal

From the comparison plots we observed that, there was good correlations for False Ashoka, Jamun and Neem in which all of them gave a slope close to 1.The slopes were satisfactory for the other two species.

According to a tree survey conducted in Chandigarh during the year 2013, the number of False Ashoka trees present was 17,057.Considering an average land area cover by the False Ashoka tree to be 4 m^2, the total uptake of ozone was calculated for the month of January 2017.PODy obtained from the model calculations was 7.7 mmol m^2 which accounted to 26.5 kg of ozone uptake by the False Ashoka trees in Chandigarh.

Chapter 4

Discussions and Conclusion

In India, the most common used metric for ozone risk assessment is AOT40 and very little study is conducted on the tree ecosystem. The AOT40 is acceptable if the plants are grown with proper supply of water and nutrients. But, when external risk factors like light gradient,water stree, the role boundary layers come into play, they can affect the plants under O_3 exposure[36].

The ozone flux into the canopy is mainly responsible for its damage and this is supported by the finding that damage to leaves is mostly around substomatal cavity[34]. This ensures that ozone flux concept is the best way to understand the damages caused by ozone in crops. But, still there is no proper understanding of whether the small high peak concentrations or low concentrations at the time of maximum physiological activity is more important. Also, measurement of the ozone fluxes are expensive and takes a lot of time. Unlike ambient O_3 concentrations, spatial data of stomatal fluxes are also not easy to obtain[35]. The best method will be to do a modelling of these conductance and ozone fluxes.

In this study we have looked into a model based study on the effect of stomatal uptake through dry deposition. The model DO3SE helped us to understand about the stomatal ozone fluxes in this location after parametrization of Temperature, Vapor pressure deficit and Solar radiation. Soil water potential is another important factor since water stress can affect the stomatal aperture. The nightime conductance values is still a question since the ambient ozone concentrations are in the range of 20-40 ppb during night. The plants respire during the night and there is flux out of leaf is the reason for which the DO3SE model does not consider the night time fluxes.

However, there are studies showing damage by night time fluxes[38]. More insight in this area is necessary.

The vegetation in urban areas are useful in many ways like by reducing temperatures,change of wind patterns,dry deposition of pollutants as well as through emission of BVOCs(biogenic volatile organic compounds) [37]. They can influence the microclimate of urban areas. In many warm and dry areas, people have studied that non-stomatal processes played a major role. Non-stomatal sinks include ozone deposition to external surfaces like stem and cuticles in parallel with with gaseous chemical losses by BVOCs[39]. Thus the study of trees in urban environment, their behaviour to ozone concentrations and other physiological factors will shed light into many pollution problems faced by the major cities. We have tried to quantify the role played by the False Ashoka trees in the city of Chandigarh.

Looking into the service done by tree cover, we must not forget the damages that can be caused by high ambient ozone concentration. Studies have proved that the ecosystem is under risk of ozone;leaf injury, decrease in photosynthesis are only symptoms. Ozone exposure metrics like AOT40, PODy give us information about ozone risk assessment. Although PODy value has a biological and mechanical advantage,most of the studies have in cooperated AOT40 values to their study.

There are 17,000 Ashoka trees in Chandigarh and the O_3 and NO_2 uptake by all these trees is calculated for the month of January. O_3 intake is 26.5 kg and NO_2 intake is 26.9 kg.These are the estimated calculations from the model that is not fully been parameterized and the tree survey took place in 2013. But, this will give us a rough estimate of the role of trees played in the urban environment.

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