Assessment of crop yield losses in Punjab using two years of continuous in-situ ozone measurements

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Certificate of Examination

This is to certify that the dissertation titled "Ozone induced crop yield loss assessment in Punjab and Haryana using real time continuous *in-situ* measurements at a site in Indo-Gangetic plain " submitted by Mr.Yash Maurya (Reg. No. MS09138) 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.Vinayak Sinha (Supervisor)   Dr. Bärbel Sinha   Prof.K.S.Viswanathan

Dated: April 25, 2014

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr.Vinayak Sinha at the Indian Institute of Science Education and Research Mohali.
This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Yash Maurya
(Candidate)
Dated: April 25, 2014

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

Dr. Vinayak Sinha
(Supervisor)

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Abstract

Tropospheric ozone is a criteria air pollutant that affects plant growth, acts as a green house gas and is toxic to humans. The harmful effects start manifesting strongly at levels greater than 30-40 ppbv. In this study we examine a high quality two year in-situ dataset of ozone at a suburban site called Mohali in the N.W. Indo-Gangetic Plain between 2011-2013. Ozone was measured using UV absorption photometry at a time resolution of 1 measurement every minute with an accuracy better than 3%, and overall uncertainty less than 6%. Quality assurance of the large dataset was accomplished by regular calibrations using a NIST traceable ozone primary standard generator and frequent zero drift tests. In order to calculate the crop yield losses, exposure metrices such as AOT40, M7, M12 and W126, of ozone, were calculated and inter-compared for the crop growing seasons of Kharif (January-March) and Rabi (July-August). The relative yield (RY) for wheat, rice, maize and cotton were calculated using ozone dose-exposure functions for these crops. The relative yield loss (RYL), crop production loss (CPL) and economic cost loss (ECL) were calculated for these crops for two financial years (2011-2012, 2012-2013) using the relative yield. The range of the total relative yield losses for the crops were as follows: wheat: 0.11-0.26 RYL; rice: 0.08-0.10 RYL; maize: 0.01-0.02 RYL; cotton : 0.03-0.10 RYL. The range of the total economic cost losses for the crops were as follows: wheat: 860.07-2355.78 Million US dollars (MUSD); rice: 355.17-424.36 MUSD; maize: 0.41-2.01 MUSD; cotton : 113.45-328.43 MUSD, respectively. The range of the total economic cost loss amounts to 1326-3110 MUSD ($\sim$ 0.5-1.1% of the All India GDP, 2009) for all four crops in Punjab and Haryana. Mitigation of high surface ozone which would require relatively little investment in comparison to economic losses incurred presently, would therefore yield massive benefits to both the national crop yield and the economy.

Chapter 1

Introduction

1.1 Literature review

1.1.1 Introduction to tropospheric ozone

Ozone (O_3) was first discovered in the the year 1840 by C. F. Schönbein. Ozone molecules absorb the harmful UV sunlight in the stratosphere and protects life on earth. In the late 1940's, Los Angeles encountered a remarkable air pollution phenomenon due to enhanced surface ozone in which 4000 deaths occured. The ambient air contained strongly oxidizing lachrymating compounds due to ozone and organic pollutants. This occurred on hot days with high solar radiation. Extensive plant damage was also observed during these pollution episodes and the impact of air pollution on agricultural crops became cause for concern. In the early 1950's, Arie Haagen-Smit and co-workers reported that such plant damage could be reproduced in the laboratory by the reaction of organic trace gases or car exhaust with nitrogen oxides NOx in presence of sunlight ([Haagen-Smit, 1952]; [Haagen-Smit and Fox, 1956]). Photochemical air pollution was first recognized in the Los Angeles, and subsequently accepted to be a world-wide problem by environmental science communities all over the world.

Tropospheric ozone causes damage to crop at elevated levels (>40 ppb). Also, tropospheric ozone is the third most powerful greenhouse gas after

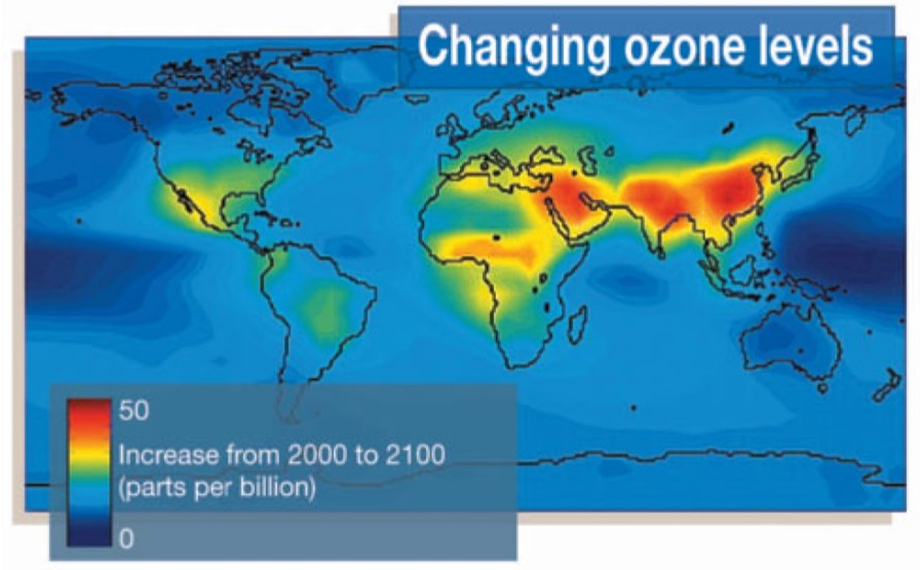

Figure 1.1: Predicted ozone surface increase from the year 2000 to 2100. [Giles, 2005]

CO_2 and CH_4 with radiative forcing value of 0.35 Watt/m^2. The elevated levels of ozone causes health problems like throat dryness, eye-irritation, reduces the volume of air that enters the lungs due to bacterial infection and inflammation [Jerrett et al., 2009]. Figure 1.1 shows the predicted surface ozone increase from the year 2000 to 2100 [Giles, 2005]. Environmental conditions are becoming increasingly worse in Indo-Gangetic Plain and its major cities are plagued with environmental problems due to unlimited population growth and unchecked vehicular emissions result in large amount of ozone precursors emissions. There is about 50 ppb of predicted ozone increase at our measurement site.

1.1.2 Sources, sinks and ambient levels of tropospheric ozone

The primary pollutants such as NOx (mainly NO_2) and volatile organic compounds (VOC), undergo photochemical reactions in sunlight to form a secondary pollutants, the most prominent of which is ozone. There are no direct emission sources of ozone in the atmosphere.

The global budget of tropospheric ozone was estimated to be 3400 - 5700 Tg/yr [Jacobs, 1999]. Out of this 3000 - 4600 Tg/yr (83%) is controlled by chemical production. Tropospheric ozone is produced when NO_2 photolyzes and the reactive oxygen atom formed combines with molecular oxygen. Peroxy radicals such as RO_2 and HO_2 can react with nitrogen monoxide NO as shown in the following reactions [R10] and [R12] followed by reactions [R2] and [R3]. Ozone production reactions [R10] and [R12] compete with the ozone loss reaction [R4]. About 400 - 1100 Tg/yr (17%) is due to the transport of ozone from the stratosphere to the troposphere. Figure 1.2 shows the sources and sinks of tropospheric ozone globally.

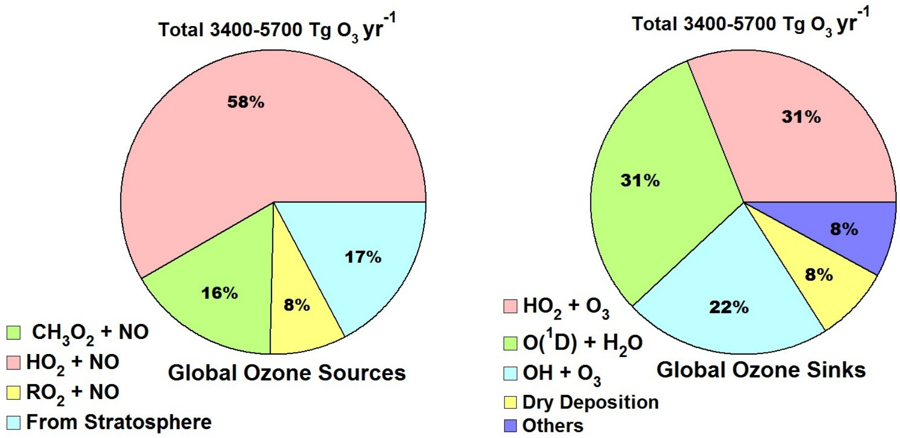

Figure 1.2: Global sources and sinks of tropospheric ozone [Source :[Jacobs, 1999]]

Loss of ozone by photolytic formation of $O(^1D)$ is followed by the formation of OH radical using H_2O. In NO_x limited regime, HO_2 and OH radical act as sink of ozone. These chemical loss processes of ozone contributes about 92% of total loss of ozone. Ozone also reacts with organic materials at the surface, known as dry deposition contributes about 8% of total loss of ozone.

Tropospheric ozone concentration is largely controlled by the chemical production and loss processes within the atmosphere.

1.1.3 Chemistry of tropospheric ozone formation in NO_x limited regime and VOC limited production regimes

Nitrogen oxides are released into the atmosphere from variety of biogenic and anthropogenic sources. Approximately 70% of the global emissions results from the combustion of fossil fuel and biomass burning which almost exclusively leads to emission directly into the planetary boundary layer, mainly in the form of NO. Before the 1950's, NO to NO_2 oxidation was thought to be due to reaction with O_2 as follows

$$2\,\mathrm{NO} + \mathrm{O_2} \xrightarrow[cm^6 molecule^{-2} s^{-1}]{k_{(298)}=2.0E^{-38}} 2\,\mathrm{NO_2} \qquad [R1]$$

The rate of reaction [R1] is strongly dependent on NO concentration. Under tropospheric condition, reaction [R1] is insignificant. The peroxy radicals such as RO_2 and HO_2 oxidise NO to NO_2 as shown in the following reactions [R10] and [R12]. In the early 1950's, Blacet showed that photolysis of NO_2 leads to a net production of O_3 commonly observed in polluted area. [Blacet, 1952]. Reaction [R2] and [R4] controls the rate of production and loss of ozone due to extremely fast reaction of conversion of O_2 to O_3 using reactive O radical.

$$\mathrm{NO_2} + h\nu \xrightarrow[cm^3 molecule^{-1} s^{-1}]{k_{(298)}=3.0E^{-14}} \mathrm{NO} + \mathrm{O(^3P)} \qquad (\lambda < 420nm) \qquad [R2]$$

$$\mathrm{O(^3P)} + \mathrm{O_2} + \mathrm{M} \xrightarrow[cm^6 molecule^{-2} s^{-1}]{k_{(298)}=6.1E^{-34}} \mathrm{O_3} + \mathrm{M} \qquad [R3]$$

$$\mathrm{NO} + \mathrm{O_3} \xrightarrow[cm^3 molecule^{-1} s^{-1}]{k_{(298)}=1.9E^{-14}} \mathrm{NO_2} + \mathrm{O_2} \qquad [R4]$$

The photolysis of ozone largely controls excited state of O radical formation and very small fraction contributes to the formation of OH radical as shown in the following reactions [R5] and [R6]. Almost 99% of the excited O radical converted to ground state of O radical through reaction [R7].

$$O_3 + h\nu \longrightarrow O_2 + O(^1D) \qquad (\lambda < 320nm) \qquad [R5]$$

$$O(^1D) + H_2O \longrightarrow 2\,OH \qquad [R6]$$

$$O(^1D) + M \longrightarrow O(^3P) \qquad [R7]$$

The peroxy radicals such as RO_2 and HO_2 are formed by OH radical initiated reaction with hydrocarbon RH in presence of O_2 as shown in the following reactions [R8] and [R9].

$$RH + OH \xrightarrow[cm^3 molecule^{-1} s^{-1}]{k_{(298)}=(0.1-7)E^{-12}} R + H_2O \qquad [R8]$$

$$R + O_2 + M \xrightarrow[cm^3 molecule^{-1} s^{-1}]{k_{(298)}=(0.8-2)E^{-11}} RO_2 + M \qquad [R9]$$

All the reactions and rate constants were taken from the book "Chemistry of the Upper and Lower Atmosphere by Barbara J. Finlayson-Pitts and James N. Pitts, Jr.". Reaction of alkyl peroxy radical with NO either leads to the formation of $RONO_2$ (with no NO_2 formation and dependent on size of alkyl group) or formation of RO radical (with NO_2 formation) as expressed in reaction [R10] dominante in atmosphere [Darnall et al., 1976]. Reaction of RO_2 radical with HO_2, RO_2 and NO_2 are alternate fates with lifetime of about 10^2, 10^4 and 10^{-1} sec. Therefore, 99.99% of RO_2 radical reacts with NO_2. The peroxy nitrates are formed by alkyl peroxy radical RO_2 with NO_2 due to thermal decomposition results in irreversible reaction leads to insignificant contribution on the RO_2 radical reaction. Reaction of alkyl peroxy radical with NO leads to the formation of RO radical and NO_2 as expressed in reaction [R10]. Similarly, reaction of hydroperoxy radical with NO leads to the formation of OH radical and NO_2 as expressed in reaction [R12]. The peroxy radicals such as RO_2 and HO_2 reacts with nitrogen oxide NO leads to the formation of NO_2 as shown in the following reactions [R10] and [R12]. The carbonyl compounds are formed by reaction of RO radical with O_2 as shown in reaction [R11]. Reaction rate of [R8],[R9], [R10] and [R12] are almost equal resulted in efficient chain propagation reactions. Production of OH by reaction [R12] is balanced by loss of OH by reaction [R8].

$$\mathrm{RO_2 + NO} \xrightarrow[cm^3 molecule^{-1} s^{-1}]{k_{(298)}=(7.5-9)E^{-12}} \mathrm{RO + NO_2} \quad \text{[R10]}$$

$$\mathrm{RO + O_2} \xrightarrow[cm^3 molecule^{-1} s^{-1}]{k_{(298)}=(4)E^{-12}} \mathrm{RCHO + HO_2} \quad \text{[R11]}$$

$$\mathrm{HO_2 + NO} \xrightarrow[cm^3 molecule^{-1} s^{-1}]{k_{(298)}=(8)E^{-12}} \mathrm{NO_2 + OH} \quad \text{[R12]}$$

Among these loss reactions, radical self reaction [R13] dominates in the NO_x limited regime due to high reaction rate of [R13] as compared to [R14] resulted in ozone production rate as shown in equation 1.1 with linear dependence on [NO_2]. Reaction [R14] dominates in the VOC limited regime due to high reaction rate of [R14] as compared to [R13] resulting in ozone production rate as shown in equation 1.2 with inverse dependence on [NO_2] and linear dependence on [RH]. HOx loss dominates by reaction [R13] in the NO_x limited regime and in the VOC limited regime is dominated by reaction [R14].

$$\mathrm{HO_2 + HO_2} \xrightarrow[cm^3 molecule^{-1} s^{-1}]{k_{(298)}=(1.7)E^{-12}} \mathrm{H_2O_2 + O_2} \quad \text{[R13]}$$

$$\mathrm{NO_2 + OH + M} \xrightarrow[cm^3 molecule^{-1} s^{-1}]{k_{(298)}=(2.2)E^{-30}} \mathrm{HNO_3 + M} \quad \text{[R14]}$$

$$P_{\mathrm{O_3}} = 2k_{(HO_2+NO)}\left(\frac{P_{\mathrm{HOx}}}{k_{(HO_2+HO_2)}}\right)^{\frac{1}{2}}[NO] \quad (1.1)$$

$$P_{\mathrm{O_3}} = \frac{2k_{(RH+OH)}P_{\mathrm{HOx}}[RH]}{k_{(OH+NO_2)}[NO_2][M]} \quad (1.2)$$

1.1.4 Causes of plant damage due to ozone exposure

Ozone impairs plant metabolism leading to yield reduction in agricultural crops and its influence on vegetation is dependent on dose, genetic background and the developmental phase of plants [Pleijel et al., 1991]. Ozone enters leaves through plant stomata during normal gas exchange in the daylight hours. Ozone reduces stomatal aperture, CO_2 uptake which leads to reduction in photosynthesis which further decreases the carbon transport to roots reducing nutrient and water uptake which finally suppresses the ability of genotype to withstand natural calmaties such as drought, flood etc. O_3 acts as a strong oxidant that alters the basic metabolic processes in plants, destroying the structure and function of biological membranes leading to electrolyte leakage causing accelerated leaf senescence and reduced photosynthesis [Calatayud et al., 2004]. The ozone induced physiological functions such as weaker and inferior crop quality resulted in decreased crop yields and economic losses ([Avnery et al., 2011b]; [Wilkinson et al., 2011]).
Wheat cultivars grown in Pakistan in filtered (O_3, NOx, SO_2, dust free air), semi-filtered(NOx, SO_2, dust free air) and ambient air(O_3, NOx, SO_2, dust in air) possess drastic difference in crop growth and biomass as illustrated in figure 1.3.

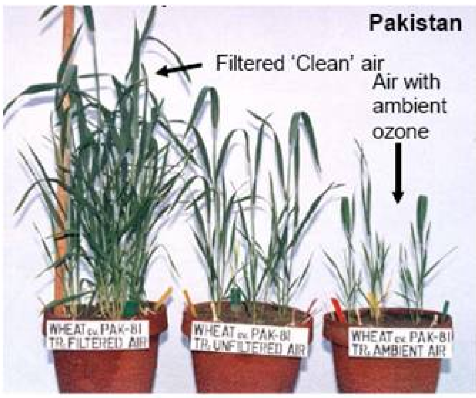

Figure 1.3: Wheat cultivars grown in Pakistan in filtered, semi-filtered and ambient air respectively possess drastic difference in crop growth and biomass [Wahid 2006]

Despite commonality in ozone induced plant damage at high levels of ozone exposure, crop sensitivity varies significantly upon the crop species, the type of cultivar, agricultural practices and various meteorological factors such as temperature, humidity, soil moisture, and radiation. Accurate result can be achieved only by in - situ experiments and field data.

1.2 Ozone induced crop yield loss assessment in Punjab and Haryana

1.2.1 Crop seasons and corresponding crops

The geographical area of India is around 2.4% of the world and contributes around 13% of the total world wheat production [Source : www.nmce.com/files/study/wheat.pdf]. Punjab and Haryana together contribute about 32% of total wheat production of India and geographical area is around 2.8% of the country. The geographical area of Punjab and Haryana is around 0.067% of the world and yet contributes about 4.16% of total wheat production of world. This clearly signifies the importance of Punjab and Haryana on global scale with respect to wheat production.

Rabi and Kharif are two different types of crop growing seasons in India, which are classified as such based depending on the time of sowing and harvesting. The Rabi crop season starts from October/November and crops are harvested in March/April (6 month crop growing season). Wheat, barley, mustard, sesame, peas etc are some examples of rabi crops. The Kharif crop season starts from July/August and crops are harvested in September/October (3 month crop growing season). Millets, paddy, maize, pulses, groundnut, red chillies, cotton, soyabean, sugarcane, turmeric etc are some examples of kharif crops [[Deb Roy et al., 2009]; www.agripb.nic.in; www.agri haryana.gov.in]. Crops of interest in the present study are wheat (Rabi); rice, maize and cotton (Kharif) and areas of interest are Punjab and Haryana.

Rice-Wheat, Cotton-Wheat, and Maize-Wheat are the major cropping systems in Punjab with cropping intensity of about 190% (piece of agricultural land is sown 1.9 times in one year on an average), implying that both Rabi and Kharif crop is grown all over the Punjab.

Wheat and rice are the most important food crops that feed the largest proportion of the world's population [Maclean, 2003]. India is the second largest wheat producing as well as consuming country of the world (after China) [Source : www.ers.usda.gov/topics/crops/wheat.aspx]. Different studies have revealed that India's actual production of wheat is estimated to be around 80% of amount needed in 2020 [www.icar.org.in], indicating the strict requirement of policies for the developments in crop production efficiency. In India, rice contributes over 43% to the nation's food grain production [Oksanen et al., 2013]. The rice demand will increase in coming decades due to increase in population and reduction in cropland area with years. Different studies have revealed that India's actual production of wheat is estimated to be around 77% of amount needed in 2020 [www.icar.org.in; www.fao.org], indicating the importance for food security of this region [Oksanen et al., 2013].

1.2.2 Historical development of ozone exposure metrics globally

The potential of ozone to damage the vegetation has been known for over 50 years and much after that its impact became a major concern in Europe and U.S.A. In the early 1980's, studies revealed that the tropospheric ozone at ambient concentrations, can cause a range of deletrious effects including visible leaf injury, growth, and agricultural crop yield reductions which was accepted by environmental science communities all over the world [Fuhrer, 1994]. The facts led to the development of policies to reduce ambient ozone concentrations. Ozone, at high concentrations can be transported over long inter continental distances which implies the policy development and implementation should essentially be on global scale. Extensive research was conducted and different approaches were taken by both United States and Europe over the same issue. They conducted many ozone crop loss assessment programmes such as Open - Top field fumigation Chambers (OTC) showing significant decrease in yield with increase in ozone concentration but after 1980's these programs were discontinued by United States [Avnery et al., 2011b]. Europe persisted with extensive research. They concluded that crop sensitivities also varies significantly depending upon the crop species, the type of cultivar and various meteorological factors such as temperature, humidity, soil moisture, and radiation.

In the context of United States, attempts to control tropospheric O_3 concentrations were primarily motivated to protect human health. Different studies revealed the adverse effect on many agricultural crops. It was later realized that, a single standard to evaluate damage to human health as well as vegetation is not optimal which led to development of many indices to evaluate crop-yield loss. Research indicates that exposure to O_3 alone results in approximately 90% of the air-pollution–induced crop loss [Heck et al., 1982]. In 1979, US EPA recognized the importance of O_3-dose/plant-response relationships for assessing the crop yield loss. Crop yield was choosen as parameter to assess the vegetation [Heck et al., 1984a]. In 1980, National Crop Loss Assessment Network (NCLAN) was the first systematic and large scale study to assess the impact of O_3 on crops in the whole world where OTC resulted in substantial reduction in crop yield with increase in ozone concentration [Heck et al., 1984b]. Initially seasonal mean and peak concentration were used but later these were replaced by the W126 and AOT40 due to the better statistical fits to the experimental yield data in the growing season [Lefohn et al., 1988]. Also preferential weightage given to daytime data was justified due to the fact that leaf stomata are open and gas exchange is maximized in daylight hours [Lee and Hogsett, 1999].

In the context of Europe, the critical level concept was proposed for use in context of policy evaluation such as mapping to identify areas where the critical level is exceeded. But due to practical limitations of mapping, it was realised that critical levels must be defined in a simpler manner [Sanderes et al]. Critical levels for ozone were first defined at a workshop at Bad Harzburg, Germany in 1988, where the values were expressed as a seasonal mean concentration. Later at a workshop at Egham, UK in 1992 it was proposed to replace this basis of expression by a cumulative exposure over a threshold concentration for a given length of time [Fuhrer et al., 1997]. At a third workshop at Bern, Switzerland in 1994, this concept was adopted and the threshold concentration was set at 40 ppb; the resulting index was termed the AOT40 (accumulated exposure over a threshold of 40 ppb). Finally, at a workshop in Kuopio, Finland in 1996, the use of the AOT40 index was agreed, and a revised set of critical level values based on this index were set for crops, forest trees, and semi-natural vegetation [Fuhrer et al., 1997]. Recent research in Europe has emphasized the development of standards that account for the variability of flux into the plant rather than just ambient O_3 concentration or cumulative exposure [Wang and Mauzerall, 2004].

In the context of Asia, studies revealed that the increased fossil-fuel combustion in Asia led to the interest in the impact of O_3 on agriculture crops. Even today, O_3 - dose/plant-response relationships developed by the United States and Europe are used to assess the crop yield loss. A study revealed that Asian grown wheat and rice cultivars are more sensitive to O_3 than the North American dose–response relationships would suggest [Emberson et al., 2009]. Still, none of Asian countries has conducted large scale studies of the effect of O_3 on crops as was conducted in the United States and Europe [Mauzerall and Wang, 2001].

1.2.3 Definition of O_3 exposure metrics

There were large number of field studies conducted to assess the adverse effect of ozone on different crops and their cultivars, especially in United States, Europe and to a lesser extent in Asia (mostly China, Pakistan and India)

[Emberson et al., 2009] which resulted in indices such as AOT40, W126 and Mx(where x=7,12).

The AOT40 (accumulated exposure over a threshold of 40 ppbv) is defined as the sum of differences between the hourly ozone concentrations and 40 ppb with global radiation greater than or equal to 50 Wm^{-2} during the crop growing season [Fuhrer et al., 1997]. The global radiation varies significantly depending upon the location, month and season of the year over different parts of the Indian geographical region. Also this global radiation threshold is observed one hour after sunrise and one hour before sunset which results in shorter length of daylight hours by approximately two hours. Therefore, with motive to give statistical importance to our result, data should be accounted as per exact timing and keeping the time duration equal [Deb Roy et al., 2009]. This time constraint did not significantly affect the AOT40 values, although projection resulted in slightly higher side, in other words, in upper limit of AOT40 value. This fact resulted in modified version of AOT40 defined as the sum of differences between the hourly ozone concentrations and 40 ppb during daylight hours (07:00-18:59 or 08:00-19:59 depending upon location of site) during the growing season. The period of daylight hours in United States and Europe are taken as 08:00-19:59 [Avnery et al., 2011b] whereas in India is taken as 07:00-18:59 for assessment of AOT40 values [Deb Roy et al., 2009].

The AOT40 metric was first proposed and adopted in Europe to assess risk to vegetation from ozone exposure. AOT40 is most widely used exposure plant response index set by the United Nations Economic Commission for Europe (UNECE), United States Environmental Protection Agency (USEPA) and World Meteorological Organization (WMO) (World Health Organization (WHO), 2000 to assess the air quality [Hollaway et al., 2012]. AOT40 has two important properties : It integrates exposure over time, for biological importance and higher weightage to higher concentrations i.e differential weighting (not apparent from definition). Despite the threshold of 40ppbv, it has an inherent property of differential weighting [Tuovinen, 2000]. Figure

1.4 shows the exponential increases of AOT40 with increase in mean O_3 concentration observed at different monitoring station in Europe, since relative yield(RY) is directly proportional to AOT40 with negative slope.

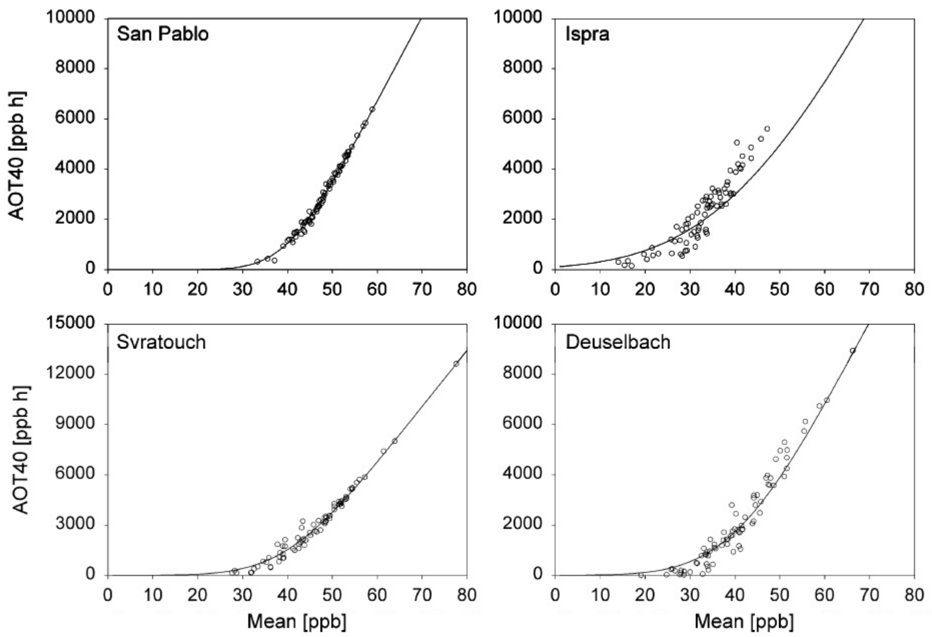

Figure 1.4: AOT40 increases exponentially with increase in mean O_3 concentration as observed at different monitoring stations in Europe. [Source : [Tuovinen, 2002]]

The W126 metric was first proposed and adopted in United States by United States Environmental Protection Agency (USEPA) to assess potential vegetation damage from ozone exposure. The W126 metric is defined as the sum of hourly ozone concentrations (weighted by a sigmoidal function) during daylight hours (07:00-18:59 or 08:00-19:59 depending upon location of site) during the crop growing season. The W126 have no threshold value as in case of AOT40 but due to sigmoidal weighting function gives more weightage to higher concentration. The W126 (similar to AOT40) emphasizes both the peak and duration of ozone concentrations exposure to vegetation [Tong et al., 2009a]. Figure 1.5 (left) shows the O_3 concentration weighting using

W126 and AOT40 indices. Figure 1.5 (right) shows the W126 and AOT40 (ppbv) indices values corresponding to O_3 concentrations (ppbv), there are two intersection between W126 and AOT40 indices at around 41.8 and 61.9 ppbv. In the interval 0 to 41.8 ppbv W126 > AOT40, from 41.9 to 61.9 ppbv AOT40 > W126 and after 61.9 ppbv W126 > AOT40 with a difference of about 40 ppbv.

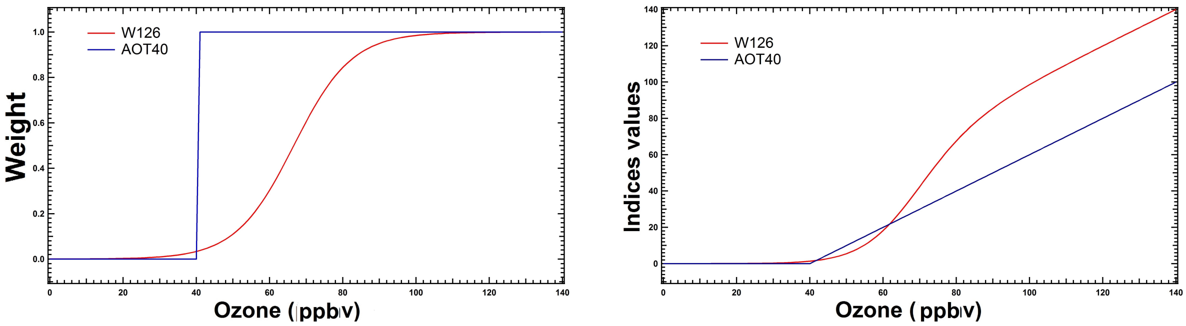

Figure 1.5: Left:Illustration of O_3 concentration weighting using continuous weighting function (W126)gives increasing weight to increasing concentrations and discontinuous weighting function (AOT40)gives equal weight to all concentrations above (weight = 1) or below (weight = 0) the threshold point, Right:W126 and AOT40 (ppbv) indices values corresponding to O_3 concentrations (ppbv)

The Mx metric is defined as the mean daytime 7 h (M7) and 12 h (M12) surface ozone concentrations during the daylight hours 09:00-15:59 and 08:00-19:59 respectively in the crop growing season [Hollaway et al., 2012]. This time window does not vary depending upon location of site and is fixed all over the world. The major difference between the Mx with AOT40 and W126 is to apply weighting to all ozone concentrations. Different studies revealed that even low O_3 concentrations can cause damage to plant leading to crop yield reductions [Heck and Colwing, 1997]. Mx metrics account for the yield losses due to ozone concentrations of even less than 40 ppbv. Therefore, Mx is preferred over AOT40 and W126 in assessing the plant damage and yield losses at low ozone concentration [Hollaway et al., 2012]. Definitions of the ozone exposure indices such as AOT40, W126, M7 and M12 used in our crop yield assessment study are shown in Table (1.1).

Table 1.1: Definitions of the ozone exposure indices used our study. n is the number of hours in the growing season, C_{O_3} is the hourly ozone concentration and i is the hour index

Index	*Definition*	*Unit*
AOT40	$AOT40 = \sum_{i=1}^{n}[C_{O_3} - 40]_i$ for $C_{O_3} \geq 40$ ppbv for 07:00-18:59 h C_{O_3}	ppb h
M7	$M7 = \frac{1}{n}\sum_{i=1}^{n}[C_{O_3}]_i$ for 09:00-15:59 h C_{O_3}	ppbv
M12	$M12 = \frac{1}{n}\sum_{i=1}^{n}[C_{O_3}]_i$ for 08:00-19:59 h C_{O_3}	ppbv
W126	$W126 = \sum_{i=1}^{n}[\frac{C_{O_3}}{1+4403exp(-0.126C_{O_3})}]$ for $C_{O_3} \geq 0$ ppmv for 07:00-18:59 h C_{O_3}	ppm h

1.2.4 Calculation of O_3 exposure metrics, relative yield loss(RYL), crop production loss(CPL) and economic cost loss(ECL)

Table (1.2) summarises the ozone exposure dose - response relationships for relative yield loss for wheat, rice, maize and cotton based on the AOT40; wheat and maize using W126; wheat and rice using M7; and finally maize using M12. Relative yield loss (RYL) is defined as the crop yield reduction from the theoretical yield that would have resulted without O_3-induced damages [Avnery et al., 2011b], calculated using equation 1.3. Crop production loss (CPL) for any crop is defined as the amount of reduction in crop production (in term of weight) due to O_3-induced damages for particular financial year. CPL is calculated using equation 1.4 for different crops.

$$RYL = 1 - RY \tag{1.3}$$

$$CPL = \frac{RYL}{1 - RYL} \times Production_{(financialyear)} \tag{1.4}$$

Economic cost loss (ECL) for any crop is defined as the amount of loss in terms of money due to O_3-induced damages for particular financial year.

Table 1.2: Ozone exposure/dose response functions for wheat, rice, maize and cotton based on the AOT40, M7, M12 and W126 indices

Crop	*Index*	*Exposure/doseresponsefunction : RY*	*Reference*
Wheat	AOT40	RY = -0.0000161 × AOT40 + 0.99	[Mills et al., 2007]
	M7	$RY = exp[-(M7/137)^{2.34}]/exp[-(25/137)^{2.34}]$(Winter)	Lesser et al.(1990)
	M7	$RY = exp[-(M7/186)^{3.2}]/exp[-(25/186)^{3.2}]$(Spring)	[Adams et al., 1989]
	W126	$RY = exp[-(W126/51.2)^{1.747}]$	[Wang and Mauzerall, 2004]
Rice	AOT40	RY = -0.0000039 × AOT40 + 0.94	[Mills et al., 2007]
	M7	$RY = exp[-(M7/202)^{2.47}]/exp[-(25/202)^{2.47}]$	[Wang and Mauzerall, 2004]
Maize	AOT40	RY = -0.0000036 × AOT40 + 1.02	[Mills et al., 2007]
	M12	$RY = exp[-(M12/124)^{2.83}]/exp[-(20/124)^{2.83}]$	[Wang and Mauzerall, 2004]
	W126	$RY = exp[-(W126/93.7)^{3.392}]$	[Wang and Mauzerall, 2004]
Cotton	AOT40	RY = -0.000016 × AOT40 + 1.07	[Mills et al., 2007]

ECL is calculated using equation 1.5 for the crops of interest. CPL is converted to ECL for different crops based on corresponding Minimum Support Prices (MSP). The MSP are recommended by Commission for Agriculture Costs and Prices (CACP) and are announced by the Government of India at the beginning of each season for each year. These prices are defined as the fixed price at which government purchases crops from the farmers. All our crops of interest come under MSP valuation process. ECL is calculated using equation 1.8 for different crops. It should be noted that MSP is approximately 50% less than the market price, which means that calculated ECL is underestimated. In other words, actual ECL is always much greater then the calculated ECL.

$$ECL = CPL \times MSP_{(financialyear)} \tag{1.5}$$

Chapter 2

Materials and Methods

2.1 Site description

All the measurements were performed using the IISER Mohali atmospheric chemistry measurement facility at IISER Mohali campus (30.667 ^{0}N - 76.729 ^{0}E, 310 m asl). A comprehensive description of the site and its representativeness for N.W. Indo Gangetic Plain chemical composition can be found in [Sinha et al., 2013]. The Indo–Gangetic plain has a very high population density and major cities like Delhi, Kanpur, Lucknow and Kolkata are located in the plain. The plain contributes large portion of the agricultural output of whole India especially in wheat and rice. The campus encloses an area of around 1.25 sq. km with 800-1000 residents. Local influence is expected to be significant only at low wind speeds (< 1 ms^{-1}). The most frequent fetch region is agricultural land use north-west of the site. In fact barring the monsoon season this is the most frequent local wind direction at the site as well.

On the basis of direction from the site, different wind sectors comprise of cities such as Chandigarh, Mohali and Panchkula spanning from North to North east of the measurement site further classified as urban sector due to the presence of urban emission sources. There are some industrial areas like Ambala, Derabassi, Yamunanagar and Zirakhpur which lie in the wind

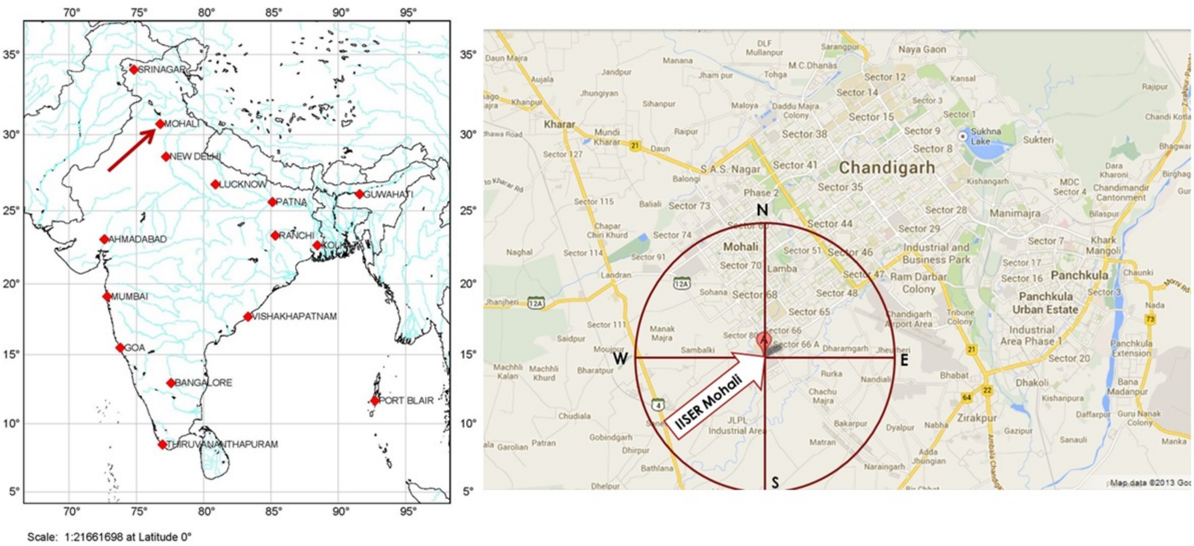

Figure 2.1: Mohali and other major Indian cities in the India map [source:Pan Map GIS software] and Our measurement site IISER, Mohali [source:www.maps.google.co.in/]

sector spanning from East to South classified as Industrial and rural sources. This sector also comprises of Ambala Chandigarh Expressway and Air Force Station hard ground. Also there are lots of Brick Kilns and other small scale industries lies in this sector. The wind sector spanning from South to North-West is dominated by agriculture activity, classified as Rural and Agricultural sector.

At the measurement site, inlets are located atop the Ambient Air Quality Station (AAQS) about 15 m above ground. A picture of the co-located inlets can be found in ([Sinha et al., 2013], Figure 4). Ambient air is drawn into the each instrument through dedicated Teflon inlet tubing with inner diameter of about 3.12 mm and length less than 5 m. To avoid the damage of instrument, dust particles are filtered at each trace gas inlet using Teflon membrane particle filters of 5 μm pore size. These Teflon membrane particle filters are changed regularly every week (in case of Monsoon season every three days), for quality assurance. The flow rate were measured by BIOS drycal definer 220 flow calibrator. The inlet residence time for the measurements of ozone is less than 6 seconds. All instrumental parameters are logged daily for data quality assurance.

2.2 Flow diagram of AAQS

The zero drift check and multi point calibration routines comprise an important part of the stringent quality control followed at the station. When the zero drift check of any analyzer is performed, dry purge air is generated using the Zero Air Generator (Thermo Scientific 1160 ZAG). The dry purge air is passed through the purafil scrubber to the calibrator. The purafil is made of aluminium oxide($\leq$ 67% by weight), potassium permanganate($\leq$ 8% by weight) and proprietary ingredients($\leq$ 26% by weight) [www.purafil.com/PDFs /MSDS/msds_purafil_EU.pdf]. The purafil scrubber removes NOx from the air. It is passed through a solenoid valve to respective analyzer.

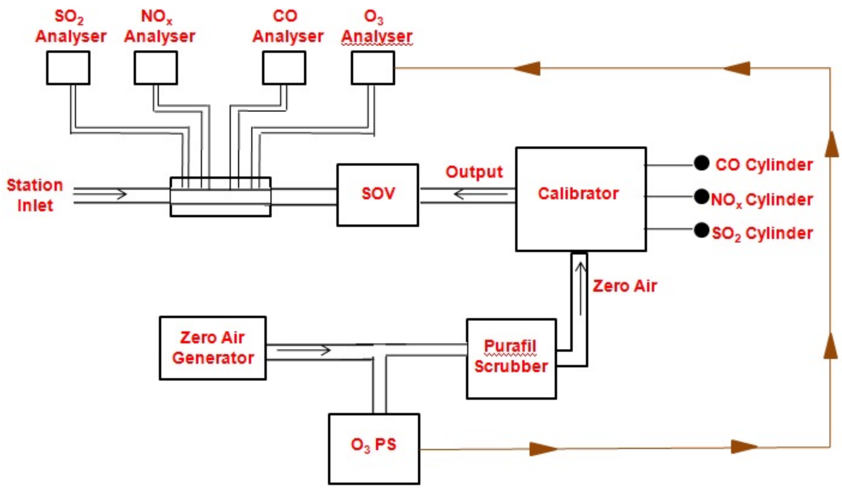

Figure 2.2: Flow diagram of Ambient Air Quality Station(AAQS) on the rooftop of CAF Buliding

When calibration of any analyzer is performed, procedure upto the calibrator is same as given above. The homogeneous mixture of dry purge air with the gas of interest for calibration. The output of calibrator path is same as given in zero drift check. When the zero drift and calibration is performed, no ambient air is passed through the sample inlet to an analyzer.

2.3 Zero Air Generator

Zero air generator(ZAG) plays a key role in quality assurance of dataset. While performing any zero drift and calibration of any analyzer, dry purge air is required which is provided by the commercial instrument "Thermo Scientific 1160 Zero Air Generator". The dry purge air is free from unwanted pollutants such as water, SO_2, O_3, NO_x, CO and VOC's.

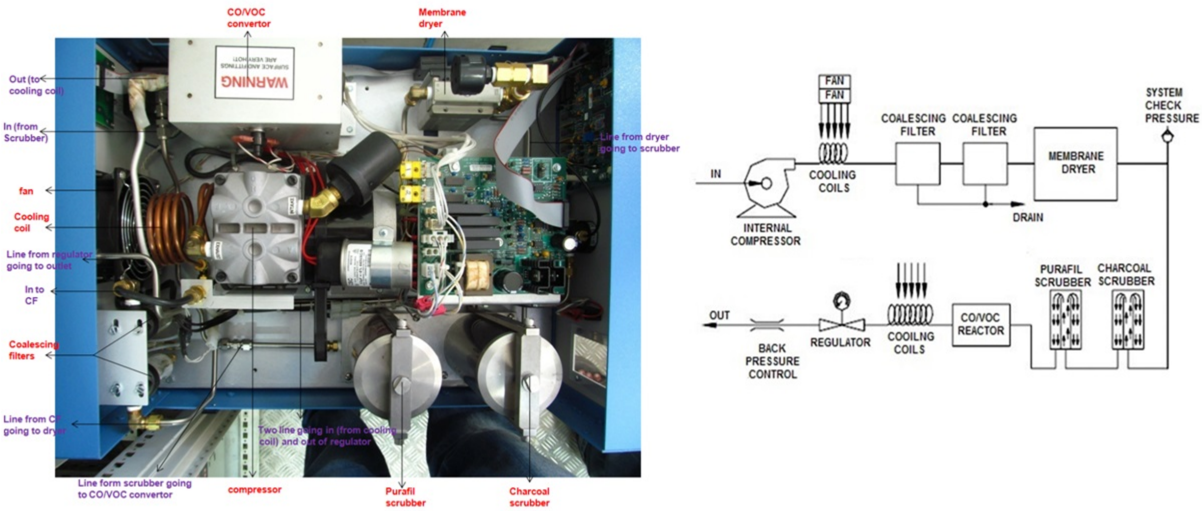

Figure 2.3: Left-Zero air generator components ; Right- Flow diagram of Zero air generator

The ZAG kept inside the Ambient Air Quality Station(AAQS) sucks the ambient air through the inlet using the internal compressor. It enters the copper cooling loop attached fan which first cool and condenses the water which is later removed by the mechanical coalescing filters and ejected out through drain. The membrane dryer further dries the air. The dry air is moved to the charcoal and purafil scrubber for removal of SO_2, O_3, NO_x. The dry purge air goes to catalytic convertor for removal of CO and VOCs and then moves to cooling coil with fan to cool the air to the room temperature. At last, regulated output of dry purge air comes out from ZAG and goes to Dynamic Gas Calibrator (DGC) when any zero drift or calibration of analyzers is performed.

2.4 Description and diagram of ozone primary standard generator

The commercial instrument "Thermo Scientific 49iPS O_3 Calibrator" dilutes in - situ generated O_3 with the zero air to desired concentration to perform the zero drift and multipoint calibration of ozone analyzer.

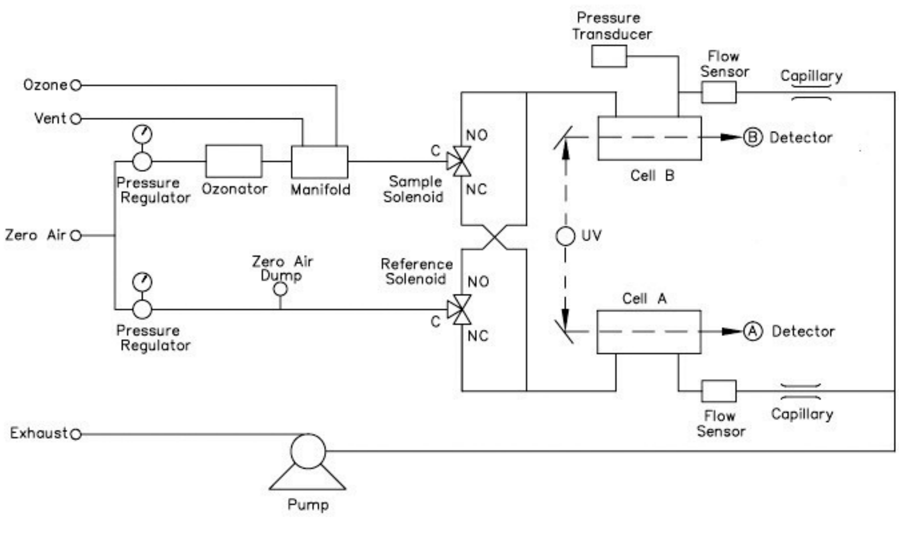

Figure 2.4: Flow diagram of ozone primary standard generator

The in - situ zero air is generated by ZAG. Zero air is sucked from the zero air bulkhead and bifurcated into two gas stream: sample gas (I) where it goes through pressure regulator, ozonator, and manifold to the sample solenoid and reference gas (I_0) where it goes through a pressure regulator to the reference solenoid. The in - situ zero air is generated by ozonator. Ground state O_2 molecule absorbs UV radiation and dissociates to form two reactive O radical. O_2 absorption maxima of UV radiation at 185 nm. The reactive O radical is reacted with O_2 molecule to form ozone. Later, a mixing chamber is used to make homogeneous mixture of zero air and ozone. The output of sample and reference gas consists of sample with ozone (actual signal) and without ozone (background signal), respectively. Hg lamp is used as 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. At last, a required amount of air goes to the ozone analyzer.

2.5 Ozone Measurements

Ambient air O_3 measurements are performed using the principle of UV absorption photometry detection principle, which is approved by the US Environmental Protection Agency (US EPA) and the Ministry of Environment and Forests, Government of India.

2.5.1 Ozone detection using UV-photometry

O_3 absorbs UV radiation and dissociates to form oxygen molecule along with O radical. O_3 absorption maxima of UV light at 254nm corresponds to electronic transition from the ground state $^1A_1$ to the excited state $^1B_2$ [Daumont et al., 1992].

$$O_3 + h\nu \longrightarrow O_2 + O \qquad (\lambda < 320nm)$$

Beer Lambert's law states that amount of absorption by ozone is directly proportional to concentration of ozone and the instrument is configured such that it operates linearly in the Beer Lambert regime for a wide dynamic range over ambient ozone levels of 1 ppb to 200 ppb. In this way, Beer Lambert's law is used to calculate ambient air ozone concentrations.

$$\frac{I}{I_o} = e^{-KLC} \tag{2.1}$$

where I = UV light intensity of sample gas
I_o = UV light intensity of reference gas
K = molecular absorption coefficient of ozone, 308 cm^{-1} (at O^0C and 1 atm)
L = length of cell, 38 cm
C = Concentration of ozone in sample air

Ambient air is sucked from the sample inlet and bifurcated into two modes: sample mode where it goes directly to the sample solenoid and reference mode where it goes through the MnO_2 based O_3 scrubber to the reference solenoid. The MnO_2 based O_3 scrubber consists of heated silver wool. The output of sample and reference mode consists of sample with ozone (actual signal) and without ozone (background signal), respectively. Hg lamp is used as 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.

2.5.2 Calibration of ozone analyzer

For ozone analyzer, the zero drift check are performed every week and five point span calibration performed every month to monitor the long term response and drift of the instrumental measurement sensitivity.

For the zero drift check, dry purge air is generated in-situ using "Thermo

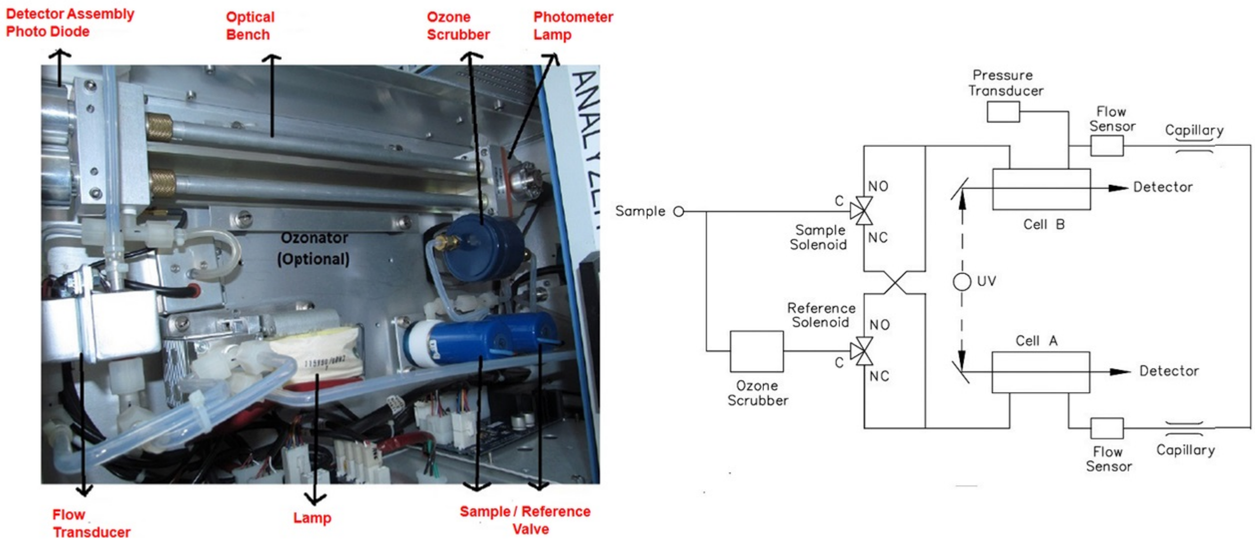

Figure 2.5: Left-Ozone analyzer components ; Right-Flow diagram of ozone analyzer [Source : Thermo Fischer Scientific 49i O_3 analyzer Instruction manual]

Scientific model 1160 ZAG". The dry purge air is passed through the external O_3 primary standard generator (PSG) "Thermo Fischer Scientific 49i PS" to ozone analyzer. The zero drift is adjusted only after atleast 30 minutes of stable response. External O_3 PSG is traceable to NIST (National Institute of Standards and Technology).

In the multipoint calibration, procedure for the zero drift check is same as given above. Ozone is generated by in-situ exposure of UV light of 185 nm on ambient oxygen using "Thermo Fischer Scientific 49i PS". Required amount of O_3 is passed for different calibration points. The pressure regulator inside the O_3 PSG is used to adjust the O_3 flow automatically . Each calibration point is accepted only after atleast 20 minutes of stable responses. Calibration curve is plotted between the measured values and the introduced concentrations of O_3. Calibration coefficient of the ozone analyzer is adjusted using the slope of the calibration curve.

Limit of detection of ozone analyzer is defined as 2σ of the stable mea-

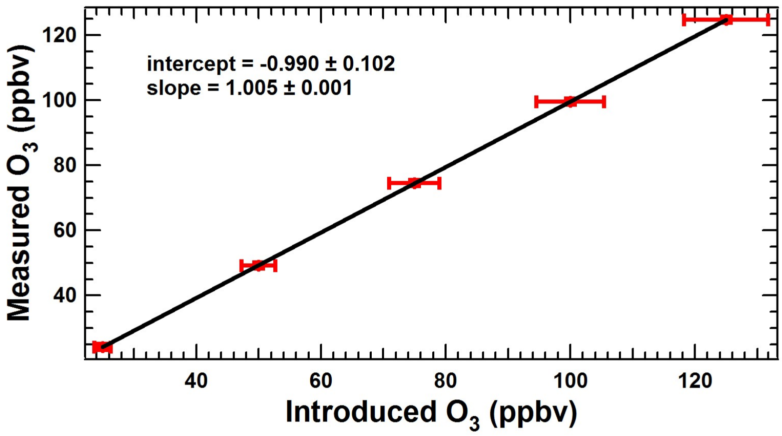

Figure 2.6: O_3 calibration plot (5 points) of Measured O_3(nmol mol^{-1}) Vs Introduced O_3(nmol mol^{-1}) on 06-09-2013. Vertical bar : precision error; Horizontal bar : accuracy error

sured values observed while sampling ozone free air. Total uncertainty of ozone analyzer calculated as the root mean square propagation of precision error 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.

$$\text{Total uncertainty} = \sqrt{(\text{precision error})^2 + (\text{accuracy error})^2} \tag{2.2}$$

In case of five - point calibration performed on 06-09-2013 as shown in figure 2.6, limit of detection was observed 0.204 ppb. The one minute data has 5.26% (4.32%(PE); 3%(AE)) uncertainty (at 25 ppbV) and 3.02% (0.34%(PE); 3%(AE)) uncertainty (at 125 ppbV). The uncertainty is inversely proportional to the ozone concentration (as expected).

It should be noted that the least square regression was performed to make the five point O_3 calibration plot as shown in Figure 2.6. However, the least square regression only takes the uncertainty in y values into account and assume that the uncertainty in x values is zero. The inherent accuracy error is always present in the x values due to the instrument uncertainty. Therefore, we performed the orthogonal distance regression with motive to analyse the affected calibration plot after including uncertainty in x values as shown in Figure 2.7. The slope of both the calibration plots vary by single digit at third decimal point. This shows that on including uncertainty of x, very minimal effect is observed on the values of calibration plot slope, which should be ignored.

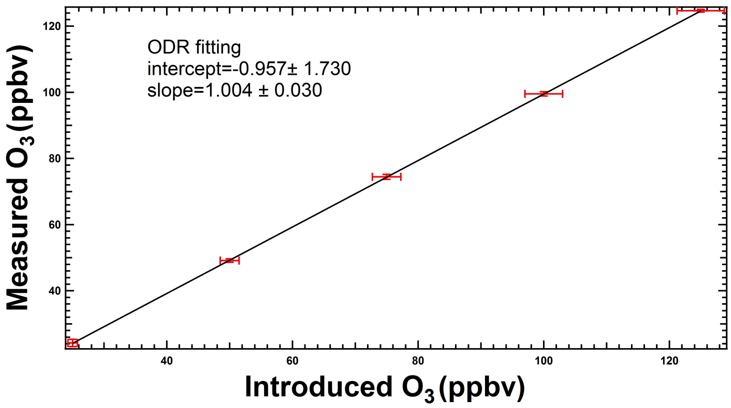

Figure 2.7: O_3 calibration plot (5 points) of Measured O_3(nmol mol^{-1}) Vs Introduced O_3(nmol mol^{-1}) on 06-09-2013 using orthogonal distance regression. Vertical bar : precision error; Horizontal bar : accuracy error

2.6 Statistical studies for the significance of variation of crop growing season ozone mixing ratio by F and T-test

ANOVA(Analyses Of Variance) was used to determine whether monthly hourly average values of ozone mixing ratio during daylight hours (07:00-18:59) of crop growing seasons has any significant variation or not month/seasonwise for the period of January 2012 to October 2013. There are three months in each seasonwise data for either Kharif or Rabi crop. We detect the variation in these three months by comparing of respective variances. To determine the same null hypothesis and alternate hypothesis technique are used.

Null hypothesis(H_0) assumes that there is no difference in monthly/seasonal hourly average O_3 mixing ratio. For comparing three month means, μ_1, μ_2, μ_3 the null hypothesis form is (H_0:μ_1=μ_2=μ_3) i.e all μ's are same. Alternate hypothesis(H_a) assumes that there is sufficient difference in monthly/seasonal hourly average O_3 mixing ratio. For comparing three month means,μ_1,μ_2,μ_3 the alternate hypothesis form is atleast two μ's should be different. If F-observed is less than or equal to critical values then it is assumed that there is no variation, implies that H_0 hold good, means accepted whereas in other case there is variation implies that H_0 does not hold good means rejected (three month data is insignificant for statistical studies). It is important to note that rejection of null hypothesis does not imply the acceptance of alternate hypothesis. The F-observed and critical values are shown in Table (3.9). In the our study, the F-critical is based on 95% confidence level ($p < 0.05$). The p values calculated for different seasons indicate the confidence is more than 95% shows that result is significant in all the eight periods i.e if p calculated value is greater than p(0.05), H_0 is accepted. This resulted in significant difference in all the eight season hourly average O_3 mixing ratio. The crop growing seasons for rabi and kharif crops resulted with these eight seasons as shown in Table 2.1. To determine the robustness of our study, t-test was used to assure the significant variation in monthly hourly average O_3 mixing ratio. T-test compare the means of two months, being three months in each seasons resulted to three results. In our analysis, there are eight seasons which resulted in twenty four results. Except for two (July 2013- September 2013 and September 2013-October 2013) all other months shows significant variation. In these two, hourly average O_3 mixing ratio are similar for both the months. But the hourly average O_3 mixing ratio are statistically different from the third month in the season (August 2013 in both the cases), which ascertain the the significant variation in F-test. The T and F-test are done for the sake of curiosity on the eight crop growing seasons. Acceptance of these tests does not have any statistical significance on these periods. Although, all the crop growing seasons are allowed to use for statistical studies.

Table 2.1: Two-way ANOVA analyses for crop growing seasons O_3 mixing ratio at p = 0.05. Where JFM is January, February, March; FMA is February, March,April; JAS is July, August, September; ASO is August, September, October.

Period (year)	**P value**	**F-observed**	**F-critical**	**Remark**
JFM (2012)	0.00	84.26	3.01	Significant
FMA (2012)	0.00	85.63	3.00	Significant
JAS (2012)	0.00	98.80	3.02	Significant
ASO (2012)	0.00	142.24	3.01	Significant
JFM (2013)	0.00	97.73	3.01	Significant
FMA (2013)	0.00	197.94	3.00	Significant
JAS (2013)	0.00	43.24	3.00	Significant
ASO (2013)	0.00	43.42	3.01	Significant

Chapter 3

Results and discussion

3.1 Results

3.1.1 Seasonal variability of diel ozone levels

Seasonal trends of surface ozone at a representative site in the N.W. Indo Gangetic Plain were analyzed using two years of in-situ data from 04.12.2011-15.10.2013. Seasonal trends enable investigation of the role of meteorology and fetch region signatures on the chemical production and transport of ozone at a site. By considering meteorology and regional emission activity in mind, there are five season such as winter, summer, monsoon, clean post monsoon and polluted post monsoon that were determined as distinct seasonal periods at the measurement site. The dates for the different seasonal periods for two years are listed in Table (3.1). Seasonal O_3 diel profile for 2011-2012 and 2012-2013 are shown in Figure 3.1. In both the years, summer season is characterized highest O_3 levels of circa 70 ppb. This is expected as favourable conditions such as high temperature, low humidity, high solar radiation favour the photochemical production of O_3 regionally. After summer, the next highest ozone levels are observed for the post monsoon seasons (both polluted and clean) with ozone levels frequently reaching 60 ppb, though there are some inter-annual differences. The post monsoon seasons are characterized by lower levels of solar radiation (maxima range ≈ 720 -480 Wm^{-2}) compared to summer season (maxima range ≈ 920-600 Wm^{-2})

Table 3.1: Dates for the different seasonal periods

Season	**Time Period**
Polluted Post Monsoon 2011	04/10/2011 - 09/12/2011
Winter 2011-2012	10/12/2011 - 29/02/2012
Summer 2012	01/03/2012 - 01/07/2012
Monsoon 2012	02/07/2012 - 18/09/2012
Clean Post Monsoon 2012	19/09/2012 - 07/10/2012
Polluted Post Monsoon 2012	08/10/2012 - 08/12/2012
Winter 2012-2013	09/12/2012 - 27/02/2013
Summer 2013	28/02/2013 - 05/06/2013
Monsoon 2013	06/06/2013 - 02/10/2013
Clean Post Monsoon 2013	03/10/2012 - 15/10/2013

but the occurrence of large scale agricultural burning emissions of ozone precursors and lower boundary layer dynamics still results in comparable high ozone levels. In the period 2011-2012 and 2012-2013, monsoon and winter shows minimum O_3 levels respectively. In the former wet scavenging of ozone precursors and lower solar radiation due to cloudy skies leads to suppressed photochemical production of O_3. In winter unfavourable conditions such as reduction in solar radiation availability, low temperature and fog resulted in less photochemical production of O_3. In general term, decreasing order of O_3 levels are as follows summer $>$ polluted post monsoon $>$ clean post monsoon $>$ monsoon $\sim$ winter.

3.1.2 Zero drift and calibration factors for two years

Zero drift checks were carried out 41 times and a multipoint span calibration was carried out 21 times during the measurement period for quality assurance of the dataset illustrated in figure 3.2.

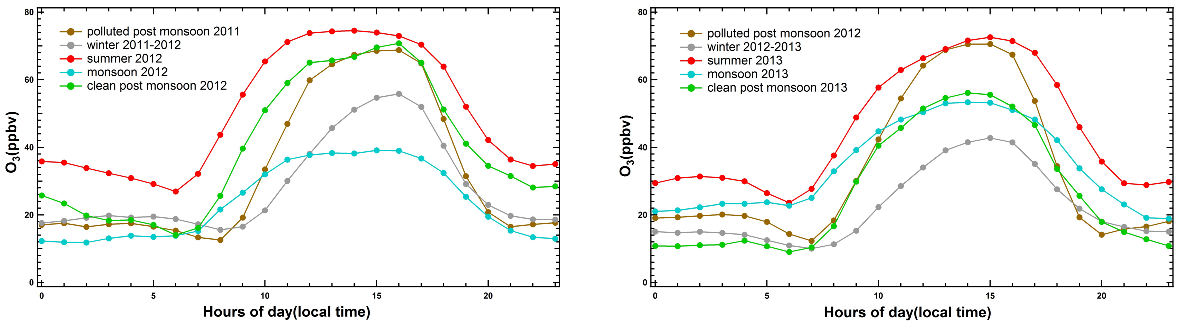

Figure 3.1: Left:Seasonal O_3 diel profile for 2011-2012 (using hourly averaged data), Right:Seasonal O_3 dial profile for 2012-2013 (using hourly averaged data)

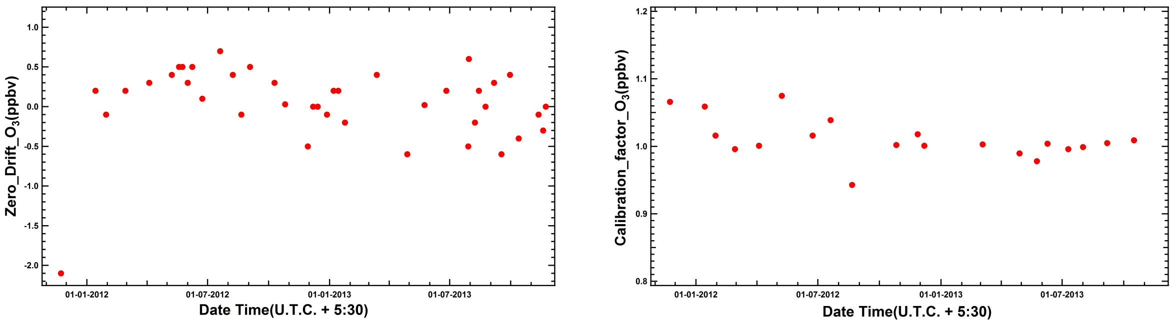

Figure 3.2: Left:Regular zero drift for ozone analyzer from 1^{st} Nov 2011 to 31^{st} Oct 2013, Right:Multi point span calibration factor for ozone analyzer from 1^{st} Nov 2011 to 31^{st} Oct 2013.

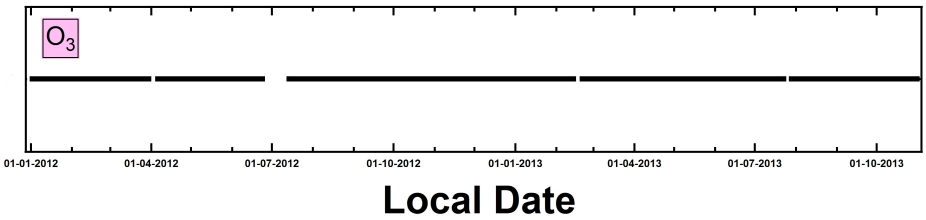

Figure 3.3: Status description of ozone ambient data from 1^{st} January 2012 to 31^{st} October 2013

3.1.3 Missing data

For any long term dataset gaps in the data are inevitable due to preventive maintenance, calibrations and technical problems that arise from time to time. For such minor missing data periods, Equation (3.1) is used to calculate the AOT40 values. Total number and percentage of missing hourly average ambient data for each month from Oct 2011 to Nov 2013 are listed in Table (3.2). Equation (3.1) can only be used with a constraint that number of measured hourly values should be $\geq 90\%$ of total possible number of hours. This constraint is fulfilled in all the months except two months July 2012 and Sep 2012. These two months lies under the Kharif 2012 crop growing season.

$$[AOT40]_{estimtated} = [AOT40]_{measured} \times \frac{Total\ possible\ number\ of\ hours}{number\ of\ measured\ hourly\ values} \quad (3.1)$$

3.1.4 Analysis of the monthly ozone exposure metrics (AOT40, W126)

Using Equation (3.1) monthly value of AOT40 and W126 indices from Dec 2011 to Nov 2013 are calculated in Table (3.3). There are three values for the indices corresponding to S.R. $\geq 50Wm^{-2}$, 07:00-18:59 and 08:00-19:59. It can be seen in Figure 3.4. Both the indices such as AOT40 and W126 tend to underestimate at S.R. $\geq 50Wm^{-2}$. For further analysis, indices values corresponding to 07:00-18:59 were used in this study. Monthly value of AOT40 and W126 indices from Dec 2011 to Nov 2013 illustrated in Figure 3.4.

Table 3.2: Total number and percentage of missing hourly average ambient data for each month from Oct 2011 to Nov 2013

Months	**Total possible number of hourly average ozone ambient data in each month**	**Total number of missing hourly average ambient data in each month**	**Percentage of missing hourly average ambient data in each month**
OCT,2011	744	75	10.08
NOV,2011	720	0	0
DEC,2011	744	3	0.40
JAN,2012	744	3	0.40
FEB,2012	696	1	0.14
MAR,2012	744	0	0
APRIL,2012	720	48	6.67
MAY,2012	744	11	1.48
JUNE,2012	720	3	0.42
JULY,2012	744	362	48.65
AUG,2012	744	71	9.54
SEP,2012	720	96	13.34
OCT,2012	744	7	0.94
NOV,2012	720	1	0.14
DEC,2012	744	32	4.30
JAN,2013	744	1	0.13
FEB,2013	672	1	0.15
MAR,2013	744	24	3.23
APRIL,2013	720	5	0.69
MAY,2013	744	3	0.40
JUNE,2013	720	12	1.67
JULY,2013	744	14	1.88
AUG,2013	744	74	9.95
SEP,2013	720	33	4.58
OCT,2013	744	42	5.64
NOV,2013	720	50	6.94

In the period from Dec 2011 to Nov 2012, the maximum values of AOT40 observed were (14292 ppb h)(May); (12172 ppb h)(June) and the minimum values of AOT40 observed were (529 ppb h)(August); (1707 ppb h)(Jan), whereas in the period form Dec 2012 to Nov 2012, the maximum values of AOT40 observed were (13119 ppb h)(May); (9190 ppb h)(June) and the minimum values of AOT40 observed were (971 ppb h)(August); (1127 ppb h)(Feb).

In the period from Dec 2011 to Nov 2012, the maximum values of W126 observed were (23782 ppb h)(May); (20261 ppb h)(June) and the minimum values of W126 observed were (504 ppb h)(August); (1541 ppb h)(Jan), whereas in the period form Dec 2012 to Nov 2012, the maximum values of W126 observed were (13119 ppb h)(May); (9190 ppb h)(June) and the minimum values of W126 observed were (823 ppb h)(August); (952 ppb h)(Feb).

It is interesting to note that the yearly maximum and minimum monthly values for both AOT40 and W126 values corresponds to the same months, May and August respectively in two years. The maximum monthly level of AOT40 reported over the IGP previously was 14 000 ppb h during October [Deb Roy et al., 2009]. In the present study value 14 292 ppb h was observed during May 2012 however this is not very remarkable as the present dataset and the dataset used in [Deb Roy et al., 2009] differ by as much as 5 years. These studies did not employ in – situ data, the model REMO-CTM was used to create the modelled data.

3.1.5 Time series plot of O_3 for two years

The National Ambient Air Quality Standard (NAAQS) exceedance limit for O_3 is 84 ppbV for 1 hour average value. In the crop growing seasons of Rabi 2012, Kharif 2012, Rabi 2013 and Kharif 2013, the number of these exceedance events were 24, 15, 14 and 30 respectively. In polluted post monsoon 2011, winter 2011-2012, summer 2012, monsoon 2012 and clean post monsoon 2012, number of these exceedance events were 37, 1, 264,

Table 3.3: Monthly value of AOT40 and W126 indices from Dec 2011 to Nov 2013.

Months	AOT40 (at S.R. $\geq 50Wm^{-2}$)	AOT40 (07:00-18:59)	AOT40 (08:00-19:59)	W126 (at S.R. $\geq 50Wm^{-2}$)	W126 (07:00-18:59)	W126 (08:00-19:59)
DEC,2011	2783	2871	2871	2809	2871	2878
JAN,2012	1607	1707	1704	1322	1541	1394
FEB,2012	2670	2695	2707	2544	2690	2556
MARCH,2012	4986	5313	5322	5691	6275	5898
APRIL,2012	6778	7323	7382	8962	9989	9444
MAY,2012	13319	14292	14531	21380	23782	22565
JUNE,2012	11403	12172	12480	17729	20261	18573
JULY,2012	2992	3137	3152	3342	3861	3438
AUGUST,2012	514	529	529	477	504	497
SEP,2012	2746	2936	2940	3175	3365	3320
OCT,2012	6259	6957	6969	8951	9709	9629
NOV,2012	4648	5025	5025	6315	6716	6636
DEC,2012	1654	1873	1885	1861	2121	2062
JAN,2013	1195	1368	1373	992	1157	1122
FEB,2013	1072	1127	1131	825	952	883
MARCH,2013	3485	3695	3705	3378	3653	3525
APRIL,2013	6627	7442	7517	8729	9894	9533
MAY,2013	12004	13119	13314	18796	21262	20206
JUNE,2013	8863	9190	9069	12445	14427	12492
JULY,2013	3168	3403	3414	3550	5774	3745
AUGUST,2013	936	971	980	756	823	792
SEP,2013	3045	3209	3240	3130	3337	3257
OCT,2013	4473	5041	5041	6036	6652	6629
NOV,2013	4342	4764	4767	5457	5905	5811

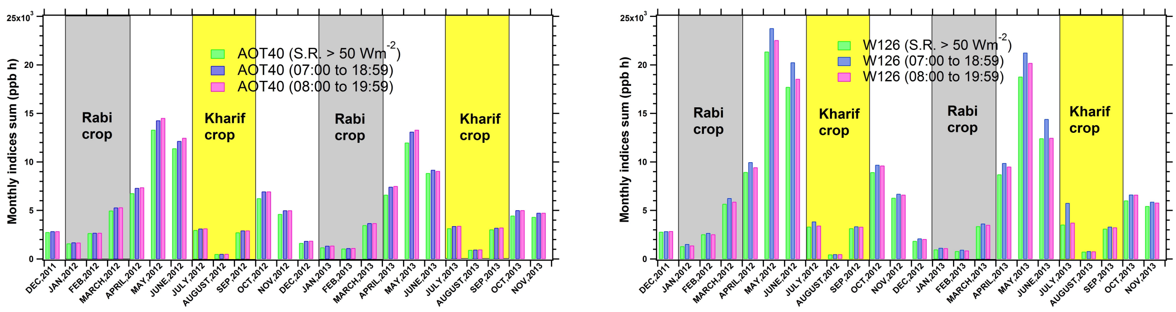

Figure 3.4: Left:Monthly value of AOT40 indices from Dec 2011 to Nov 2013, Right:Monthly value of W126 indices from Dec 2011 to Nov 2013

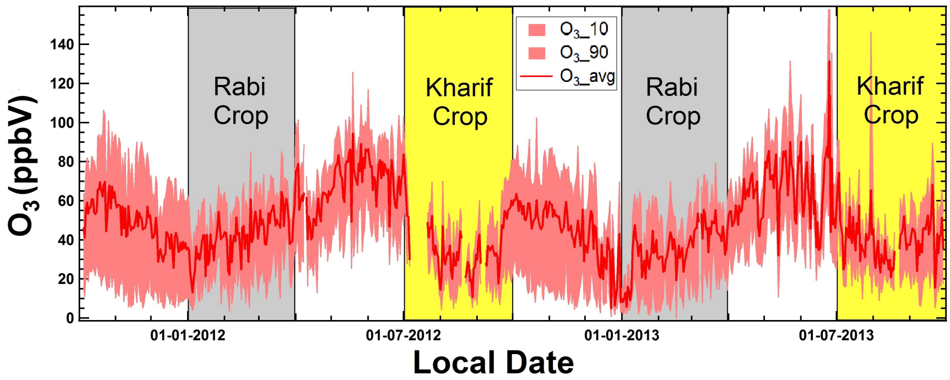

Figure 3.5: Daily time series plot using hourly average value of O_3 mixing ratio in time window of 07:00 to 18:59 from Oct 2011 to Oct 2013. Shaded region represents hourly variability (10^{th} and 90^{th} percentile)

0 and 3 respectively. In polluted post monsoon 2012, winter 2012-2013, summer 2013, monsoon 2013 and clean post monsoon 2013, number of these exceedance events were 37, 1, 264, 0 and 3 respectively. Daily time series plot using hourly average value of O_3 mixing ratio in time window of 07:00 to 18:59 from Oct 2011 to Oct 2013 is shown in Figure 3.5.

3.1.6 Crop yield and economic losses due to elevated O_3 based on present work

Rabi and Kharif are two different types of crop seasons prevalent in North India. The Rabi crop season starts from October/November and is harvested in March/April (6 month crop growing season) while the Kharif crop season starts from July/August and is harvested in September/October (3 month crop growing season). For determining O_3 induced crop yield loss assessment, "growing season" is defined as the 3 months prior to the start of the harvest period [Avnery et al., 2011a]. (For wheat, potential grain yield is solely determined before heading but actual grain yield is primarily dependent on the amount of starch that ultimately fills the spikelets, mostly determined by other stages of crops such as growth and reproduction (National Consortium of SRI(NCS) 2013)). Hence, in this work we calculated O_3 exposure crop yield loss considering the last 3 months of the crops. Thus, the actual growing seasons here for Rabi are: January/February - March/April and for Kharif: July/August - September/October. For the O_3 induced crop yield loss assessment in Punjab and Haryana, we found temporal variability in the crop growing seasons on spatial scales. To account for this, we use a sowing time period for each crop season such motive that all the sowing time possibilities are covered. Therefore, Period 1 and Period 2 for Rabi crops were from 1^{st} Jan - 31^{st} March and 1^{st} Feb - 30^{st} April respectively, whereas for Kharif crops were from 1^{st} July - 30^{st} Sep and 1^{st} August - 31^{st} October respectively.

Keeping this in mind two periods were define for each crop in each financial year to calculate the upper and lower limit of O_3 induced relative yield loss (RYL), crop production loss (CPL) and economic cost loss (ECL). Period 1 and Period 2 for wheat crop is from 1^{st} Jan - 31^{st} March and 1^{st} Feb - 30^{st} April (3 month growing season), respectively whereas for Rice, Maize and Cotton are from 1^{st} July - 30^{st} Sep and 1^{st} August - 31^{st} October (3 month growing season), respectively for two financial years (2011-2012 and 2012-2013).

Table 1.2 summarizes the ozone exposure/dose response functions for wheat, rice, maize and cotton. Relative yield for each crop is calculated based on the ozone exposure - dose response relationships compiled in Table 1.2, which gives linear exposure-response relationships as a function of AOT40 for the crops. It gives exponential decreasing exposure-response relationships as a function of W126 exposure indices for wheat and maize.

Table 3.4 summarizes the relative yield loss and relative yield loss percentage for wheat, rice, maize and cotton. Relative yield for each crop is calculated using the Equation (1.3). Period 1 and period 2 for wheat, rice, maize and cotton consisted with different exposure indices for three month crop growing season. It is important to note that relative yield loss for period 2 is greater than period 1 based on all the used exposure indices for wheat,

rice, maize and cotton. It is due to the fact that kharif season monthly values for all the indices in October > July, similarly in rabi season monthly values of all the indices in April > January.
Table 3.5 summarizes the crop production for wheat, rice, maize and cotton reported by state government of Punjab and Haryana. The decreasing order of crop production (million kilograms) are as follows wheat > rice > cotton > maize for Punjab and Haryana.

Table 3.6 summarizes the crop production loss and crop production loss percentage for wheat, rice, maize and cotton, separately for Punjab and Haryana. Crop production loss for each crop is calculated using the Equation (1.4) and crop production data compiled in Table 3.5.
Table 3.7 summarizes the Minimum support price (MSP) per kilogram for wheat, rice, maize and cotton reported by state government of Punjab and Haryana. The decreasing order of MSP (rupees) are as follows cotton > wheat > rice > maize for financial year 2012-2013. It is important to note that MSP reported by government for any crop is about 50 % less than the market price.

Table 3.8 summarizes the relative yield loss, crop production loss and economic cost loss range calculated for wheat, rice, maize and cotton, separately for Punjab and Haryana. Economic cost loss for each crop is calculated using the Equation (1.5), MSP for each crop as shown in Table 3.7 and crop production loss for wheat, rice, maize and cotton compiled in Table 3.6.

The maximum crop production loss for wheat are 6213 (Mkg) for Punjab and 4515 (Mkg) for Haryana account for 25.68 % RYL using AOT40 index annually. This resulted with maximum Wheat ECL for Punjab and Haryana about 69589 (MRs) and 50576 (MRs) annually corresponding to the financial year 2011-2012.
The minimum crop production loss for wheat are 369 (Mkg) for Punjab and 247 (Mkg) for Haryana account for 2.18 % RYL using W126 index annually. This resulted with minimum Wheat ECL for Punjab and Haryana about

Table 3.4: Relative yield loss and relative yield loss percentage calculated for wheat, rice, maize and cotton based on the AOT40, M7, M12 and W126 indices from Nov 2011 to Oct 2013. Period 1 and Period 2 for wheat crop is from 1^{st} Jan - 31^{st} March and 1^{st} Feb - 30^{th} April (3 month growing season) respectively whereas for Rice, Maize and Cotton are from 1^{st} July - 30^{th} Sep and 1^{st} August - 31^{st} October (3 month growing season)respectively for two financial years (2011-2012 and 2012-2013)

Crop	**Index**	**Period 1**	**RY**	**RYL**	**RYL%**	**Period 2**	**RY**	**RYL**	**RYL%**
Wheat (2011-2012)	AOT40(07:00-18:59)	9715	0.83	0.17	16.64	15331	0.74	0.26	25.68
	M7(Winter)	45.06	0.94	0.06	5.40	52.36	0.92	0.08	8.30
	W126(07:00-18:59)	10.50	0.94	0.06	6.09	18.95	0.84	0.16	16.16
Rice (2012)	AOT40(07:00-18:59)	6602	0.91	0.09	8.56	10422	0.90	0.10	10.06
	M7	40.38	0.99	0.01	1.30	46.98	0.98	0.02	2.13
Maize (2012)	AOT40(07:00-18:59)	6602	0.99	0.01	0.36	10422	0.98	0.02	1.74
	M12	38.54	0.97	0.03	3.05	42.78	0.96	0.04	4.26
	W126(07:00-18:59)	7.73	0.99	0.01	0.02	13.57	0.99	0.01	0.15
Cotton (2012)	AOT40(07:00-18:59)	6602	0.96	0.04	3.57	10422	0.90	0.10	9.68
Wheat (2012-2013)	AOT40(07:00-18:59)	6190	0.89	0.11	10.97	12264	0.79	0.21	20.75
	M7(Winter)	39.96	0.96	0.04	3.66	49.87	0.93	0.07	7.25
	W126(07:00-18:59)	5.76	0.98	0.02	2.18	14.50	0.89	0.11	10.45
Rice (2013)	AOT40(07:00-18:59)	7583	0.91	0.09	8.95	9221	0.90	0.10	9.59
	M7	43.41	0.98	0.02	1.66	46.51	0.98	0.02	2.07
Maize (2013)	AOT40(07:00-18:59)	7583	0.99	0.01	0.72	9221	0.98	0.02	1.32
	M12	40.97	0.96	0.04	3.71	42.01	0.96	0.04	4.12
	W126(07:00-18:59)	9.93	0.99	0.01	0.05	10.81	0.99	0.01	0.07
Cotton (2013)	AOT40(07:00-18:59)	7583	0.95	0.05	5.13	9221	0.92	0.08	7.75

Table 3.5: Total Crop production for wheat, rice, maize and cotton reported by state government of Punjab and Haryana for two financial years where Mkg (million kilograms)[source : http://nfsm.gov.in/Presentations/10NFSMEC/PUNJAB.ppt; http://agricoop.nic.in/imagedefault/Rabi2013/Punjab/Punjab.ppt]

Place (year)	**Wheat (MKg)**	**Rice (MKg)**	**Maize (MKg)**	**Cotton (MKg)**
Punjab (2012-2013)	17982	11374	475	1627
Punjab (2013-2014)	16591	10815	562	1635
Haryana (2012-2013)	13069	3745	19	2373
Haryana (2013-2014)	11117	3536	21	2314

Table 3.6: CPL and CPL% calculated for wheat, rice, maize and cotton based on the AOT40, M7, M12 and W126 indices from Nov 2011 to Oct 2013. P1 and H1 are period 1 for Punjab and Haryana respectively, whereas P2 and H2 are period 2 for Punjab and Haryana respectively

Crop	**Index**	**CPL (P1)**	**CPL% (P1)**	**CPL (P2)**	**CPL% (P2)**	**CPL (H1)**	**CPL% (H1)**	**CPL (H2)**	**CPL% (H2)**
Wheat (2011-2012)	AOT40(07:00-18:59)	3589.50	19.96	6213.37	34.55	2608.78	19.96	4515.77	34.55
	M7(Winter)	1026.46	5.71	1627.60	9.05	746.01	5.71	1182.91	9.05
	W126(07:00-18:59)	1166.12	6.48	3465.99	19.27	847.51	6.48	2519.02	19.27
Rice (2012)	AOT40(07:00-18:59)	1064.76	9.36	1272.21	11.18	350.58	9.36	418.89	11.18
	M7	149.81	1.31	247.54	2.17	49.33	1.31	81.50	2.17
Maize (2012)	AOT40(07:00-18:59)	1.72	0.36	8.41	1.77	0.07	0.36	0.34	1.77
	M12	14.94	3.14	21.13	4.44	0.60	3.14	0.84	4.44
	W126(07:00-18:59)	0.09	0.02	0.71	0.15	0.01	0.02	0.03	0.15
Cotton (2012)	AOT40(07:00-18:59)	60.53	3.70	175.23	10.71	87.85	3.70	254.32	10.71
Wheat (2012-2013)	AOT40(07:00-18:59)	2044.29	12.32	4344.01	26.18	1369.80	12.32	2910.76	26.18
	M7(Winter)	630.30	3.80	1296.87	7.82	422.34	3.80	868.98	7.82
	W126(07:00-18:59)	369.74	2.23	1936.08	11.67	247.75	2.23	1297.29	11.67
Rice (2013)	AOT40(07:00-18:59)	1063.09	9.82	1147.17	10.60	347.58	9.82	375.07	10.60
	M7	182.56	1.68	228.60	2.11	59.69	1.68	74.74	2.11
Maize (2013)	AOT40(07:00-18:59)	4.07	0.72	7.52	1.33	0.15	0.72	0.28	1.33
	M12	21.65	3.85	24.15	4.29	0.81	3.85	0.90	4.29
	W126(07:00-18:59)	0.28	0.05	0.39	0.07	0.01	0.05	0.01	0.07
Cotton (2013)	AOT40(07:00-18:59)	87.98	5.40	136.68	8.40	125.13	5.40	194.40	8.40

Table 3.7: Minimum support Price (MSP) for wheat, rice, maize and cotton reported by state government of Punjab and Haryana for two financial years for each crop used for Economic Cost Loss (ECL) assessment where Rs./kg means Rupees per kilogram [source:http://cacp.dac.net.nic.in.MSP.pdf]

Financial year	**Wheat (Rs./kg)**	**Rice (Rs./kg)**	**Maize (Rs./kg)**	**Cotton (Rs./kg)**
2011-2012)	11.20			
2012-2013	12.85	12.80	11.75	39.00
2013-2014		13.45	13.10	40.00

Table 3.8: Relative yield loss, Crop production loss and Economic cost loss range calculated for wheat, rice, maize and cotton based on the AOT40, M7, M12 and W126 indices from Nov 2011 to Oct 2013 where CPL and ECL units are million Kilograms(MKg) and million rupees(MRs) respectively.

Crop	**Index**	**RYL**	**CPL (Punjab) (Mkg)**	**CPL (Haryana) (Mkg)**	**ECL (Punjab) (MRs)**	**ECL (Haryana) (MRs)**
Wheat (2011-2012)	AOT40(07:00-18:59) M7(Winter) W126(07:00-18:59)	0.17- 0.26 0.05- 0.08 0.06- 0.16	3589.49- 6213.37 1026.45- 1627.59 1166.12- 3465.99	2608.78- 4515.76 746.01- 1182.90 847.51- 2519.02	40202.41- 69589.74 11496.35- 18229.12 13060.54- 38819.24	29218.33- 50576.62 8355.32- 13248.59 9492.17- 28213.02
Rice (2012)	AOT40(07:00-18:59) M7	0.08- 0.10 0.01- 0.02	1064.75- 1272.20 149.80- 247.53	350.58- 418.88 49.32- 81.50	13628.92- 16284.28 1917.56- 3168.49	4487.44- 5361.75 631.37- 1043.25
Maize (2012)	AOT40(07:00-18:59) M12 W126(07:00-18:59)	0.01- 0.02 0.03- 0.18 0.00- 0.01	1.72- 8.41 14.94- 21.13 0.09- 0.71	0.07- 0.34 0.60- 0.84 0.01- 0.02	20.16- 98.83 175.58- 248.33 1.11- 8.38	0.80- 3.95 7.02- 9.93 0.04- 0.33
Cotton (2012)	AOT40(07:00-18:59)	0.03- 0.10	60.53- 175.23	87.85- 254.32	2360.68- 6833.97	3426.24- 9918.67
Wheat (2012-2013)	AOT40(07:00-18:59) M7(Winter) W126(07:00-18:59)	0.11- 0.21 0.04- 0.07 0.02- 0.10	2044.29- 4344.01 630.29- 1296.87 369.74- 1936.07	1369.80- 2910.76 422.33- 868.98 247.75- 1297.29	26269.12- 55820.65 8099.34- 16664.77 4751.21- 24878.62	17601.93- 37403.26 5427.06- 11166.44 3183.61- 16670.17
Rice (2013)	AOT40(07:00-18:59) M7	0.09- 0.10 0.01- 0.02	1063.08- 1147.17 182.55- 228.60	347.58- 375.07 59.68- 74.74	14298.56- 15429.43 2455.41- 3074.69	4674.95- 5044.71 802.80- 1005.28
Maize (2013)	AOT40(07:00-18:59) M12 W126(07:00-18:59)	0.01- 0.02 0.03- 0.04 0.01- 0.02	4.07- 7.52 21.65- 24.15 0.28- 0.39	0.15- 0.28 0.81- 0.90 0.01- 0.01	53.39- 98.48 283.66- 316.35 3.68- 5.15	1.99- 3.67 10.59- 11.82 0.13- 0.19
Cotton (2013)	AOT40(07:00-18:59)	0.05- 0.08	87.97- 136.68	125.12- 194.40	3519.13- 5467.44	5005.08- 7776.04

4751 (MRs) and 3183 (MRs) annually corresponding to the financial year 2012-2013.

The maximum crop production loss for rice are 1272 (Mkg) for Punjab and 418 (Mkg) for Haryana account for 10.06 % RYL using AOT40 index annually. This resulted with maximum rice ECL for Punjab and Haryana about 16284 (MRs) and 5361 (MRs) annually corresponding to the financial year 2011-2012.
The minimum crop production loss for rice are 149 (Mkg) for Punjab and 49 (Mkg) for Haryana account for 1.03 % RYL using M7 index annually. This resulted with minimum rice ECL for Punjab and Haryana about 1917 (MRs) and 631 (MRs) annually corresponding to the financial year 2011-2012.

The maximum crop production loss for maize are 21.13 (Mkg) for Punjab and 0.84 (Mkg) for Haryana account for 10.76 % RYL using M12 index annually. This resulted with maximum Wheat ECL for Punjab and Haryana about 248 (MRs) and 10 (MRs) annually corresponding to the financial year 2011-2012.
The minimum crop production loss for maize are 0.09 (Mkg) for Punjab and 0.01 (Mkg) for Haryana account for 0.02 % RYL using W126 index annually. This resulted with minimum maize ECL for Punjab and Haryana about 1.11 (MRs) and 0.04 (MRs) annually corresponding to the financial year 2011-2012.

Large range of crop production loss for wheat and rice using M7 and W126 indices for the both financial years was observed. Both the crops appears resistant (acc. to M7 metric) and appears extremely sensitive (acc. to AOT40 metric). It is due to the fact that wheat and rice are more sensitive to frequent exposure to high O_3 concentrations (better captured by AOT40 metric) than to long-term exposure to moderate O_3 concentrations (better captured by M7 metric) leads to variances in result. In othere case, Maize appears sensitive (acc. to M12 metric) and appears resistant (acc. to AOT40 metric). It is due to the fact that maize is more sensitive to long-term expo-

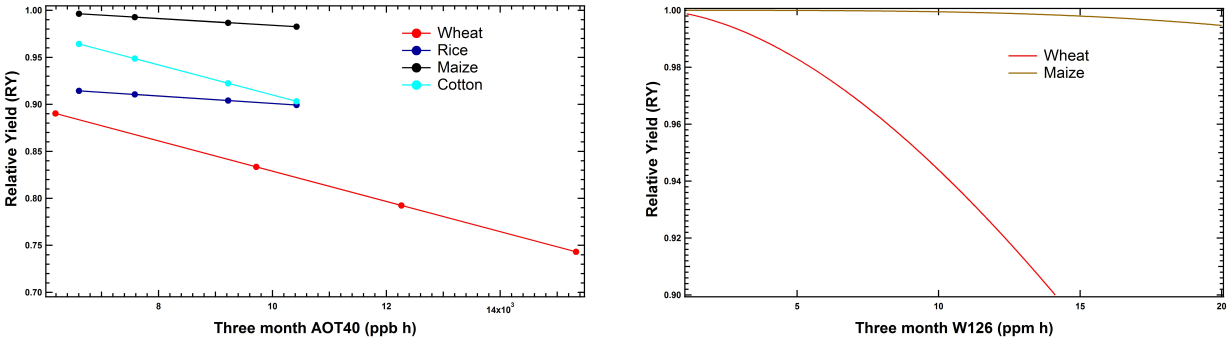

Figure 3.6: Left:Illustration of different sensitivity of wheat, rice, maize and cotton using three month AOT40(ppb h), Right:Illustration of different sensitivity of wheat, rice, maize and cotton using three month AOT40(ppm h)

sure to moderate O_3 concentrations (better captured by M12 metric) than to frequent exposure to high O_3 concentrations (better captured by AOT40 metric) leads to variances in result.

This shows that different crop have different sensitivity factor such as cultivar type, pollutants, agricultural practices and various meteorological factors etc leads to significant difference in sensitivity towards higher ozone levels. Wheat and rice are more sensitive to frequent exposure to high O_3 concentrations than to long-term exposure to moderate O_3 concentrations whereas maize is is more sensitive to long-term exposure to moderate O_3 concentrations than to frequent exposure to high O_3 concentrations. The comparison for cotton is not possible due to the unavailability of Mx exposure relationship. Figure 3.6 shows the different sensitivity of crops due to high ozone levels using three month AOT40 and W126 indices. The decreasing order of crop sensitivity due to elevated ozone levels are as follows : Wheat > cotton > rice > maize.

Table 3.9: CPL and ECL comparision for wheat based on the M7 and AOT40 indices where CPL and ECL units are million metric tons(MMT) and million US dollars(MUSD) respectively.[Sources : [a][Debaje, 2014],[b][Avnery et al., 2011a], [c][Avnery et al., 2011b]]

Place	CPL (M7) (MMT)	ECL (M7) (MUSD)	CPL (AOT40) (MMT)	ECL (AOT40) (MUSD)
Uttar Pradesh (2002-2007 mean)[a]	2.64	375	9.41	1336.7
Punjab (2002-2007 mean)[a]	2.04	289.8	7.3	1037
Haryana (2002-2007 mean)[a]	1.24	176.1	3.6	511.4
Madhya Pradesh (2002-2007 mean)[a]	0.75	106.5	2.68	380.7
Rajasthan (2002-2007 mean)[a]	0.85	120.7	3.06	434.7
Bihar (2002-2007 mean)[a]	0.48	68.2	1.73	245.7
Maharashtra (2002-2007 mean)[a]	0.13	18.5	0.43	61.1
Gujarat (2002-2007 mean)[a]	0.07	9.9	0.09	12.8
West Bengal (2002-2007 mean)[a]	0.08	11.4	0.27	38.3
Uttaranchal (2002-2007 mean)[a]	0.09	12.8	0.31	44
India (2002-2007 mean)[a]	8.60	1221.6	28.8	4091
India 2000[b]			16 - 32	3200 - 6400
India 2030[c]			32 - 64	6400 - 12800
Punjab 2012(our study)	1.02 - 1.62	258.3 - 409.7	3.58 - 6.21	903.6 - 1564.1
Haryana 2012(our study)	0.74 - 1.18	187.7 - 297.7	2.60 - 4.51	656.7 - 1136.7
Punjab 2013(our study)	0.63 - 1.29	182 - 374.5	2.04 - 4.34	590.4 - 1254.6
Haryana 2013(our study)	0.42 - 0.86	121.9 - 250.9	1.36 - 2.91	395.6 - 840.7

3.1.7 Comparison of crop yield and economic losses due to elevated O_3

CPL and ECL measurements all over the world for wheat based on the M7 and AOT40 indices are listed in Table 3.9. The last four rows corresponds CPL and ECL for Punjab and Haryana for two financial years based on our present work. On comparing second and third row with last four rows, we found that our present work CPL range for wheat based on the M7 and AOT40 indices is less than the recent assessments published in the literature [Debaje, 2014]. The ECL's are higher by 43.13% (M7) 54.90% (AOT40), respectively in comparison to the same literature. It is due to the fact that their study is based on the MSP from 2002-2007 and our study uses the MSP of 2012 and 2013 which leads to higher estimates. It is important to note that their studies did not employ in–situ data. Based on 2 years of continuous in–situ ozone data, in this work the CPL and ECL for wheat in Punjab and Haryana are calculated to be (2.47 MMT)(CPL) ; (667 MUSD)(ECL) using M7 and (8.98 MMT)(CPL) ; (2398 MUSD)(ECL) using AOT40.

3.2 Comparative analysis with measurements from other sites in the world

Figure 3.7 shows the AOT40 measurements map over the India in increasing order of longitude. The maximum three months AOT40 values corresponds to Pune about 25437 (ppb h) (Jan-March), due to favourable conditions such as high temperature, high solar radiation and high levels of ozone precursors favour the photochemical production of O_3 regionally. The minimum three months AOT40 values corresponds to Pune about 63 (ppb h) (July-September), due to wet scavenging of ozone precursors and lower solar radiation due to cloudy skies leads to suppressed photochemical production of O_3 regionally. The three months AOT40 values for Ahmednagar and Delhi are 3575-9150 (ppb h) and 3700-14100 (ppb h), respectively. The three months AOT40 values from our present work at IISER, Mohali are shown for crop growing seasons. The three month AOT40 values at IISER, Mohali ranges from 6190 (ppb h) (Jan-March 2013) - 15331 (ppb h) (Feb-April 2012). The decreasing order of maximum three months AOT40 values assessed at different sites are as follows : Pune > Mohali > Delhi > Ahmednagar.

3.3 Implications

3.3.1 Suggested solution to increase crop yield

- EDU (ethylene diurea; [N-(2-2-oxo-1-imidazolidinyl) ethyl]-N'-phenyl urea) is a chemical protectant against ozone, can be used to suppress ozone injuries in several crop plants but not implemented in fields to grow crops due to lack long term toxicology tests [Oksanen et al., 2013]. The actual mechanism of action of EDU is still not fully understood, but EDU is suggested to prevent ozone injuries by up-regulating antioxidative defense responses, and by membrane protection through suppressing the formation of reactive oxygen species [Singh et al., 2009]. The cost of 10 gm of EDU is about 560 USD, this makes the imple-

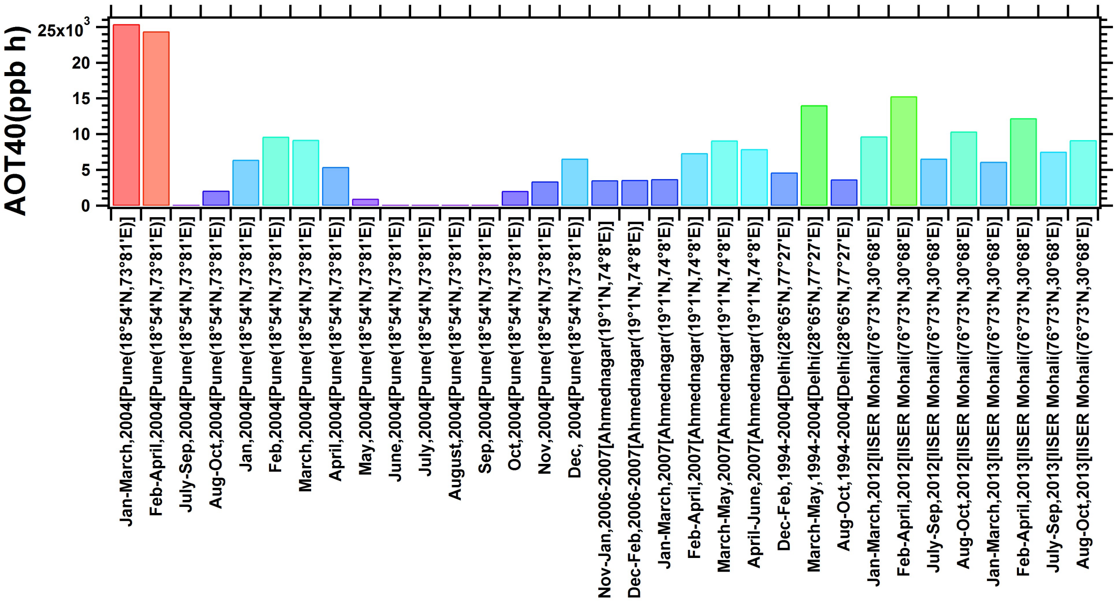

Figure 3.7: AOT40 measurements map over the India in increasing order of longitude. References are as follows Ahmednagar [Debaje et al., 2010]; Pune [Beig et al., 2008];Delhi [Ghude et al., 2008].

mentation of EDU impossible in the fields to grow crop.

- Semi dwarf and hybrids of different cultivars should be replaced with traditional cultivars of different crops, this replacement have played significant roles in China's successful increase food production [Zhang, 2011].

- By reducing surface O_3 concentrations provide an excellent opportunity to increase global crop yields, research should be done to determine and mitigate decrease the peak concentration of surface O_3 regionally.

- Farmers are unaware about the adverse effect of ozone,

3.3.2 Suggested solution to accurate crop yield assessment

- Crop production data are solely dependent on the amount of crop received in grain market reported by different agriculture department (statewise) which leads to underestimation of production of all the crops, since a large unknown portion is consumed before going to grain market. Knowing the exact production of each crop will lead to more accurate assessment of crop yield loss due to ozone exposure.

- There is lack of real time continuous *in-situ* measurement of ozone in our area of interest Punjab and Haryana. More spatial and long term coverage of *in-situ* ozone measurements would be better to assess crop and economic losses.

- Even today, assessments of the magnitude of ozone risk to agriculture in Asia rely on O_3-dose/plant-response relationships developed by the United States and Europe are used to assess the crop yield loss, crop sensitivity varies significantly upon the crop species, the type of cultivar, other pollutants, agricultural practices and various meteorological factors such as temperature, humidity, soil moisture, and radiation. Accurate result can be achieved only by local experiments and data. None of Asian country government including India has conducted such a large-scale study of the effect of O_3 on crops, barring some studies [Mahapatra et al., 2012]. Conducting the large scale field study of different crops for our region will lead to more precise O_3-dose/plant-response relationships and result in accurate crop yield loss assessments relevant to Indian region.

- In our region of study, large range of cultivars are grown of each crop which possess different sensitivity towards ozone. Cultivars with higher resistance to ozone should be identified and encouraged.

3.3.3 Comparison of United states, Europe and Asian exposure-response data for assessment of crop yield loss by ozone

Assessments of the magnitude of ozone risk to agriculture in Asia rely on O_3-dose/plant-response relationships developed by the United States and Europe are used to assess the crop yield loss leads to the assumption that United States, Europe and Asia crops response to ozone for local cultivars, pollutants and other conditions are identical which is not true. Many experiments such as fumigation and filtration are conducted in Asian countries such as China, India and Pakistan on wheat and rice crop species with motive of comparison with United States and Europe dose–response relationships. The Asian data shows that at ambient O_3 concentrations (which vary between ~35–75 ppb (4–8 h growing season mean), yield losses for wheat and rice range between 5–48 and 3–47% respectively whereas United States and Europe dose–response relationships suggested the 5-20% yield loss for these crops [Emberson et al., 2009]. Asian countries such as China, India and Pakistan crop species are comparable in terms different crop sensitivity factors. It is clear that Asian grown wheat and rice cultivars are more sensitive to O_3 than the United States and Europe dose–response relationships would suggest. Our two year data shows that at ambient O_3 concentrations (which vary between ~45–56 ppb and ~41-49 ppb (8 h growing season mean) leads to yield losses for wheat and rice range between 10–43 and 8–45% respectively whereas United States and Europe dose–response relationships suggested the 11-26 and 8-10% yield loss for wheat and rice respectively. There is clear underestimation of crop yield loss assessment in Asia when risk assessment is done using the United States and Europe dose–response relationships. RYL, CPL and ECL all are intercorrelated to each other, underestimation of RYL leads to underestimated CPL and ECL values.

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