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# Air pollution effect of O3 on crop yield in rural India

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#### 1. Introduction

Surface ozone (O<sub>3</sub>) is the most important secondary air pollutant that negatively affects human health and agriculture crops yield [1-4]. Many studies detailed the reduction of crop yield and photosynthesis by exposure to O<sub>3</sub> [5,6 and references therein]. The National Crop Loss Assessment Network (NCLAN) program set out to study the effects of O<sub>3</sub> on crop yield using open-top chambers throughout the USA [7], while a European Open-Top Chambers Program (EOTCP) provided a similar study in Europe [8]. NCLAN results indicate a reduced annual soybean yield of 10% and a reduced cotton yield of 12% for seasonal mean O<sub>3</sub> mixing ratios greater than 50 ppbv [9]. Fuhrer et al. [8] modeled a reduction of yield with increasing O<sub>3</sub> over a 40 ppbv threshold, resulting in a 10% reduction in spring wheat yield for  $O_3$  mixing ratios in southern Europe. Different O<sub>3</sub> indices that account for threshold effects include the AOT40, SUM06, and W126 indices. The AOT40 index is the sum of the amounts by which hourly O<sub>3</sub> mixing ratios exceed a threshold of 40 ppbv over the growing season and during daylight hours. The SUM06 is the sum of the hourly O<sub>3</sub> mixing ratios over 60 ppbv over the growing season and during daylight hours. The AOT40 and SUM06 index have commonly been used to estimate crop loss due to O<sub>3</sub> in Europe and USA, respectively. The W126 index weights each hourly value by a sigmoidal weighting scheme, so the low O<sub>3</sub> values are not completely ignored. Pleijel et al. [10] compared a number of these indices for wheat and potatoes and concluded that the threshold-based flux index best captured O<sub>3</sub> damage to

## ABSTRACT

Measurement of surface ozone ( $O_3$ ) mixing ratio was made from January 2006 to December 2007 in Ahmednagar ( $19.1^{\circ}N$ ,  $74.8^{\circ}E$ , 657 m above sea level), India. The monthly average of daytime maximum of  $O_3$  mixing ratio ranged from 14 to 57 parts per billion by volume (ppbv) with an annual average of about 20 ppbv. The estimated winter wheat and summer crop yield reduction by 10% and 15%, respectively from present  $O_3$  pollution level associated with AOT40 (accumulation exposure of  $O_3$  concentration over a threshold of 40 ppbv) index values 7370-9150 ppbv h in rural areas.

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crop yield. Several studies have shown that present  $O_3$  pollution in India can damage the vegetation and reduce the agricultural crop yields by about 5–20% as per the AOT40 (accumulation exposure of  $O_3$  concentration over a threshold of 40 ppbv) index [4,11–14]. These studies have revealed that the AOT40 value is above the critical level (3000 ppbv h) for daylight over 3 months period during growing to harvesting season of crop. Model studies by Mittal et al. [11] and Engardt [12] have shown that the monthly mean of  $O_3$ mixing ratio ranges between 30 and 45 ppbv for the year 2000 and AOT40 values above critical levels over the Indian region during winter and summer season. The model values of these two studies show that mixing ratios of  $O_3$  are in agreement with the measured values of  $O_3$  in both urban and rural sites in India [15,16].

In India, a few  $O_3$  measurements studies have been performed. They have shown that high  $O_3$  mixing ratio between 34 and 151 ppbv during winter and summer season in urban areas [15,17–22]. Naja and Lal [22] reported that  $O_3$  mixing ratio was increase at the rate of 1.45% year<sup>-1</sup> during 1954–55 and 1991–93 in Ahmedabad. However, there are very few  $O_3$  measurements available in rural areas [16,23,24].

In this study, we present diurnal and seasonal variation of  $O_3$  measured at rural site-Ahmednagar in the light of meteorological conditions. Preliminary assessment of the effects of  $O_3$  pollution on winter wheat and summer crops yield reduction associated with AOT40 index is discussed.

#### 2. Ozone formation

The anthropogenic emissions of  $O_3$  precursors such as nitrogen oxides ( $NO_x = NO + NO_2$ ) and volatile organic compounds (VOC) across Asia also increased, in particular over the Indian and Chi-

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nese region [25]. The photolysis of  $O_3$  (at wavelengths < 319 nm) produces excited singlet (O(<sup>1</sup>D)) oxygen atom. The reaction of oxygen atom with water vapor (H<sub>2</sub>O) forms two hydroxyl (OH) radicals [26]:

$$O_3 + h\upsilon \rightarrow O_2 + O(^1D) \tag{R1}$$

$$O(^{1}D) + H_{2}O \rightarrow 2OH$$
(R2)

where hv represents the energy of a photon depend upon the intensity of incoming solar radiation (ISR).

The oxidation of VOC by OH radical produces hydroperoxyl radicals (HO<sub>2</sub>) or peroxy organic radicals (RO<sub>2</sub>) (where R is the organic group). The reaction of HO<sub>2</sub> or RO<sub>2</sub> radicals with nitric oxide (NO) produces nitrogen dioxide (NO<sub>2</sub>) when NO mixing ratios > 30 parts per trillion by volume (pptv) (critical level) is present in the ambient air [26]:

$$VOC + OH \rightarrow HO_2 + CARB$$
 (R3)

$$NO + HO_2 \rightarrow NO_2 + OH$$
 (R4)

The reaction of OH radical with VOC produces the intermediate carbonyl compounds, denoted by CARB, which further oxidizes by OH radical, producing again HO<sub>2</sub> and RO<sub>2</sub> in the subsequent cycles. If NO mixing ratio less than critical level in environment, O<sub>3</sub> titration occurred by NO (R7). The photolysis of NO<sub>2</sub> (at wavelengths <424 nm) produces ground-state (O) oxygen atoms, which further formed O<sub>3</sub> by reacting with the oxygen molecule (O<sub>2</sub>) in the troposphere:

$$NO_2 + h\upsilon \rightarrow NO + O$$
 (R5)

$$O + O_2 + M \rightarrow O_3 + M \tag{R6}$$

where M (usually  $N_2$  or  $O_2$ ) represents a molecule that absorbs the excess vibrational energy and thereby stabilizes the  $O_3$  molecule formed. In short,  $O_3$  production is a complex and non-linear process in which  $NO_x$  acts as a critical precursor.

A way of removing O<sub>3</sub> is its reaction with NO and dry deposition:

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{R7}$$

 $NO_2 + OH \rightarrow HNO_3$  (R8)

$$\mathrm{HO}_2 + \mathrm{HO}_2 \to \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 \tag{R9}$$

This catalytic photochemical  $O_3$  production cycle has a major ratedetermining pathway (R3), which produces  $HO_2$  and  $RO_2$  in the presence of OH and VOC; and reaction (R4), which produces  $NO_2$ from NO,  $HO_2$  and  $RO_2$ . Photolysis of  $NO_2$  leads to  $O_3$  production (R5), while,  $NO_2$  oxidation (R8) and  $HO_2$  self-oxidation (R9) terminate the cycle.

### 3. Location of site and measurement techniques

#### 3.1. Description of site

Fig. 1 presents a map of India with the measuring site-Ahmednagar, and a few other major populated cites which are located around it and are mentioned in the present study. The sampling site of  $O_3$  is surrounded by cultivated field and some small and big trees. There are no major emission sources of air pollution in the vicinity of sampling site, while state highway is approximately 1 km away. Present population of Ahmednagar (19.1°N, 74.8°E, 657 m above sea level) is about 0.4 millions as per 2001 India census and vehicular population nearly 0.05 millions [27]. However, several major highly populated and polluted cities are located around the Ahmednagar. Aurangabad is the nearest metropolitan urban city located at about 80 km in the northeast direction and Pune in southwest direction at 115 km away with moderate industrial background for both cities. The vehicular population was about



**Fig. 1.** Map of India shows the ozone measurements site-Ahmednagar and some other adjacent major cites used in the study.

2 millions in Pune in 2007 and rank fifth, while Mumbai rank second in total number of vehicles in India. Mumbai is located about 150 km away from Ahmednagar in the northwest direction having highest number of taxies plying on road in India along with strong chemical and petrochemical industrial background and emits large amount of O<sub>3</sub> precursors. The winter crop sown season start during November–January and harvest period in March–April over the region. Wheat and onion are the major winter crops, while in summer vegetables and fruits (watermelon) varieties also grown till June, all these crops are ozone-sensitive [13].

#### 3.2. General meteorology

Inter-tropical Convergence Zone moves forward towards north from June to September bringing lot of moisture and rains by southwesterly strong winds from the Arabian Sea (clean air masses void of pollutants) across the Indian subcontinent known as southwest (SW) monsoon season (hereafter SW monsoon). The SW monsoon (June-September) covers almost all Indian states including the present O<sub>3</sub> measurements site-Ahmednagar in Maharashtra state. The annual normal RF (RF refers to rainfall) is 62 cm of which major RF about 80-90% occurs during the SW monsoon at Ahmednagar (http://www.imd.gov.in). Fair weather with onset of winter conditions prevails in October and November known as post SW monsoon season with prevailing moderate winds from NE direction expected to bring polluted air masses (NO<sub>x</sub>, VOC, O<sub>3</sub>) to the present O<sub>3</sub> measurement site-Ahmednagar from north and northeastern Indian states [24]. The highest temperature was observed in April and May due to intense ISR. Details of the general meteorology of the region are given elsewhere [24].

#### 3.3. Measurement techniques

Brewer electrochemical ozone sensor developed at India Meteorological Department (IMD) was used to measure surface ozone  $(O_3)$  in parts per billion by volume (ppbv). The procedure of operation, the working principle of the instrument and other details are given by Sreedharan and Tiwari [28]. O<sub>3</sub> was continuously measured by electrochemical ozone sensor (KI method) all 24 h during the study period. The accuracy of the measurements has been estimated to be  $\pm 10\%$ . The lower detection limit of the KI method is 1 ppbv and the precision better than  $\pm 2\%$ . The data can be recorded by the ozone sensor with the resolution of 1 min. In this study, we used KI method for measurements of O<sub>3</sub> because of absence of other direct measurements techniques (ultraviolet (UV) photometric ozone analyzer) and cost constraints. The measurements of  $O_3$  by KI method were compared with  $O_3$  measured by UV analyzer (Model O<sub>3</sub> 42 M, Environment S.A., May 2002) run simultaneously. The correlation coefficient change for all the calibration sets range from 0.86 to 0.96. The average correlation coefficient is found to be 0.90. The differences in two techniques of O<sub>3</sub> measurements under ambient condition were less than 10%.

In this study, all  $O_3$  analyses are based upon the hourly average data, Indian Standard Time (IST). IST is 05:30 h plus Greenwich Mean Time (IST = UTC + 05:30 h).

The hourly mean of  $O_3$  mixing ratio was calculated from the 10 min averaged data. The daily mean of  $O_3$  was calculated from the hourly average of  $O_3$  mixing ratio of 24 h. The monthly average of  $O_3$  was calculated from the available daily mean of  $O_3$  mixing ratio for each month. The maximum of  $O_3$  was a single peak value of the daytime around noon. The average monthly daytime maximum of  $O_3$  was calculated from averaging daily single maximum values of  $O_3$  mixing ratio for each month. The monthly diurnal means are computed by averaging for all days of a month for specific hour.

#### 4. Results and discussion

#### 4.1. Diurnal variation

Fig. 2a shows the comparison of annual average diurnal variations of  $O_3$  mixing ratio observed in 2006 and 2007 with  $1\sigma$ standard deviation. Annual diurnal average of O<sub>3</sub> was computed for specific hours from January to December. In April, the highest of  $O_3$  was observed; hence it is investigated separately in Fig. 2b. It is seen from Fig. 2a that the O<sub>3</sub> mixing ratio starts increasing after sunrise in the morning, attains maximum during daytime due to photochemical production (R1)-(R6) and then again decreases until the next morning. The O<sub>3</sub> reaches to maximum value at noon due to large photochemical production by intense ISR. The O<sub>3</sub> mixing ratio decreases after noon as the intensity of ISR reduces ((R1) and (R5)) results in the slowdown of the O<sub>3</sub> production. Annual diurnal variation of O3 shows the maximum mixing ratio of O3  $30.9\pm10.9$  and  $33.2\pm19.8\,ppbv$  around  $13:00\text{--}15:00\,h$  at noon in 2006 and 2007, respectively. The corresponding minimum of O<sub>3</sub> mixing ratio  $8.5 \pm 4.6$  and  $9.3 \pm 9.8$  ppbv was observed at about 07:00 h in the morning (Fig. 2a). During nighttime, production of O<sub>3</sub> ceases due to lack of sunlight and hence O<sub>3</sub> decreases throughout the nighttime by chemical loss of O<sub>3</sub> with NO (R7) and to a lesser extent with nitrate radical  $(NO_3)$ , and dry deposition at the surface.

Fig. 2b shows the comparison of average monthly diurnal variation of  $O_3$  in April 2006 and 2007 during the summer season (March–May) when the highest  $O_3$  mixing ratio was observed. The production of  $O_3$  was more in April during the summer season because of highest ambient temperatures, more intense ISR ((R1) and (R5)), less cloudy and longer (>13 h) duration of day, which enhanced the photochemistry resulting high mixing ratio of  $O_3$ . It is seen from the Fig. 2b that the maximum of  $O_3$  mixing ratio was about 68.5 ppbv around 14:00 h at noon and minimum about 34.6 ppbv at 07:00 h in the morning indicating that the  $O_3$  mixing ratio was highest during daytime and also in the nighttime in April 2007. The highest  $O_3$  peak in April 2007 was due to favorable tem-



**Fig. 2.** Annual average diurnal variations of ozone mixing ratio (ppbv) observed at Ahmednagar for 2006 and 2007 (a) and average diurnal variations of ozone mixing ratio in April 2006 and April 2007 (b). Note that *Y*-axis scale is different for b.

perature and abundance of intense ISR promoting photochemical reactions of O<sub>3</sub> production. The hot temperature in April mean that the chemical reactions proceed at a faster rate and O<sub>3</sub> production was close to its greatest. On the contrary, RF and overcast sky conditions was persist in April 2006 that diminished ISR at the surface leads to low O<sub>3</sub> mixing ratio 36.9 ppbv at 13:00 h and 6.7 ppbv at 07:00 h in the morning. This indicates that O<sub>3</sub> in April 2006 reduced drastically nearly by half at daytime and five times in the morning compared to  $O_3$  in April 2007 despite sufficient its precursor (particularly  $NO_x$ ) due to RF and overcast sky condition persisting for more number of days (Table 1). Similar results were reported from our previous study over this region that the O3 reduces drastically if cloud cover (CC) increases [24]. In other study by Reddy et al. [16] was reported similar diurnal cycle of O<sub>3</sub> at rural site as observed in the present study. The altitude of the Ahmednagar station is 657 m above sea level, which is within the atmospheric boundary layer height indicates that tropospheric ozone intrusion in the ground-level has to be ruled out. Further, the latitude of Ahmednagar (19.1°N) station lies in the tropics. Hence, stratospheric ozone intrusion in the troposphere at the ground-level is also ruled out [29]. Therefore, high O<sub>3</sub> during summer is only due to both local photochemical production of O<sub>3</sub> and transport of O<sub>3</sub> from upwind northeast and northwest cities.

#### 4.2. Variation of ozone with meteorological parameters

Table 1 shows the monthly average  $O_3$  mixing ratio with meteorological parameters: maximum temperature ( $T_{max}$ ), minimum temperature ( $T_{min}$ ), relative humidity (RH), CC, RF and wind speed

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Month	2006								2007							
	O <sub>3</sub> (ppbv)	$T_{\min}$ (°C)	$T_{\max} (^{\circ}C)$	RH (%)	CC (%)	RF (mm)	WD (°)	WS ( $ms^{-1}$ )	O <sub>3</sub> (ppbv)	$T_{\min} (^{\circ}C)$	T <sub>max</sub> (°C)	RH (%)	CC (%)	RF (mm)	WD (°)	WS $(ms^{-1})$
January	21	10.2	30.7	54	0	0	z	1.8	13.9	10.4	30.5	65	0	0	z	2
February	20.2	13	33.7	46	12	0	MNW	2.1	21.9	11.4	32	52	0	0	MNW	2.2
March	22	17.5	35.4	45	16	e	NW	2.4	29.8	14.3	36.2	39	0	0	NW	2.3
April	27.8	19.7	39	31	25	10	NW	ŝ	53	20.2	39.5	30	0	0	NW	3.4
May	24.1	24.4	29.6	31	27	11	N	3.6	38.8	23.4	39.5	42	40	2	N	3.9
June	18.3	22.8	33.8	69	38	261	SW	3.9	7.4	22	33	71	80	218	SW	4.1
July	13.3	22.1	27.9	79	85	61	SW	4.5	7.1	21.9	29.4	75	81	93	SW	4.7
August	14.7	20.9	27.3	79	87	130	SW	4.2	8.7	21.9	29.1	74	88	237	SW	4.4
September 11.3	20.5	29.6	79	83	346	SW	c	8.8	21.2	29.4	81	76	213	SW	3.6	
October	19	17.1	32	68	60	50	NE	2.5	17.1	17.2	32.1	58	20	0	NE	2.8
November 18	12.9	29.5	67	50	46	NE	2.3	23.1	14.4	30.8	63	10	0	NE	2.5	
December	13.7	12.1	30.1	67	0	0	NNE	1.4	18.9	13.4	30.4	62	0	0	NNE	2
r <sub>min</sub> – average minii	num temperat	ture and T <sub>max</sub> -	- average may	ximum tem	perature.											

Comparison of O<sub>3</sub> mixing ratio and meteorological conditions observed during 2006 and 2007 at Ahmednagar.

Comparison of monthly average of O<sub>3</sub> mixing ratio and meteorological conditions observed during 2006 and 2007 at Ahmednagar.

Table 1

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(WS) and wind direction (WD) observed during 2006 and 2007 at Ahmednagar. The highest  $O_3$  mixing ratio 27.8 and 53 ppbv in April, while lowest 11.3 ppbv in September and 7.1 ppbv in July during 2006 and 2007, respectively. It is seen from Table 1 that average highest *T*<sub>max</sub> 39 and 39.5 °C was observed in April 2006 and 2007, respectively, while lowest  $T_{\min}$  about 10 °C in January in both the years. In our previous study, Debaje and Kakade [24] reported that high O<sub>3</sub> mixing ratio in April over this region is related to the highest  $T_{\text{max}}$  and intense ISR. The average RH, CC and RF are highest during SW monsoon while their values are lowest during the summer season for both years. However, it is also observed from Table 1 that duration of CC was longer in 2006 from February to November and RF from March to November. On the contrary, duration of CC was shorter in 2007 from May to November and RF from May to September. This indicates that less cloudy and rainy days were in 2007 as compared to in 2006. Similarly, the more annual RF in 2006 was 918 mm, while it was 763 mm in 2007 which was above the annual normal RF in both the years. The more CC and RF are mostly responsible for generating low O<sub>3</sub> mixing ratio during 2006. The annual average of  $O_3$  mixing ratio was 18.6 ppbv in 2006 and 20.7 ppbv in 2007 indicating annual average O<sub>3</sub> was higher in 2007 by 2.1 ppbv. The average WD was NW in April, SW from June to September and NE in October and November was the same roughly for both the years. The average highest WS was  $4-5 \,\mathrm{m \, s^{-1}}$  during SW monsoon and lowest (calm) wind  $1-2 \,\mathrm{m \, s^{-1}}$ in winter season (December-February), while moderate WS was  $2.2-2.8 \text{ m s}^{-1}$  observed in October and November.

#### 4.3. Seasonal variation

Fig. 3a and b shows the comparison of seasonal average of diurnal variations of O<sub>3</sub> in summer, SW monsoon, post SW monsoon (October-November) and winter season observed during 2006 and 2007, respectively. The seasonal averages are computed from their respective months, for example, averaged of O<sub>3</sub> for March to May considered as a summer season, and so on. Fig. 3a and b shows that seasonal differences in amplitude of the diurnal O<sub>3</sub> cycle in 2006 and 2007, respectively. The amplitude of O<sub>3</sub> was highest in summer and lowest in SW monsoon. The maximum of O<sub>3</sub> 37.8 ppbv was observed around 16:00-17:00 h in the evening and minimum of 8.3 ppbv at 07:00 h in the morning during summer season in 2006 (Fig. 3a). During SW monsoon, maximum of O<sub>3</sub> 18.5 ppbv was observed at 16:00 h and minimum 8.9 ppbv at 07:00 h. The rains wash out large amount of peroxyl radicals  $(HO_2 \text{ and } RO_2)$  (R4) due to higher solubility which results in the gas phase photochemistry of O<sub>3</sub> production become strongly inactive [26]. The O<sub>3</sub> mixing ratio values in post SW monsoon and winter season lies between the O<sub>3</sub> values in summer and SW monsoon 2006. On the contrary, highest maximum of O<sub>3</sub> mixing ratio 57.3 ppbv was observed around 15:00 h and minimum 20.4 ppbv at 07:00 h during summer season in 2007 (Fig. 3b). The corresponding lowest O<sub>3</sub> mixing ratio 11.7 and 4 ppbv was observed during SW monsoon. The comparison of daytime O<sub>3</sub> show that daytime O<sub>3</sub> during summer season in 2007 was higher by approximately 1.5 times related to clear sky condition than  $O_3$  in 2006.

#### 4.4. AOT40 index calculations

AOT40 (AOT40 is the hourly mean  $O_3$  mixing ratio accumulated over a threshold  $O_3$  mixing ratio of 40 ppbv during daylight hours, units ppbv h) is calculated as the sum of the differences between the hourly mean  $O_3$  mixing ratio (in ppbv) and 40 ppbv when the mixing ratio exceeds 40 ppbv during daylight hours, accumulated over a time period of 3 months. A number of measures have been developed to assess the detrimental effects of  $O_3$  on natural and cultivated crops [30–32]. All these measures are mixing ratio-based



Fig. 3. Seasonal average diurnal variations of ozone mixing ratio (ppbv) observed for (a) 2006 and (b) 2007.

and are based on the mixing ratios occurring during the sunlit hours of the vegetation, when plants are actively taking up  $O_3$  along with carbon dioxide ( $CO_2$ ) during photosynthesis [4,12,13]. Stomatal conductance is higher in hot, humid environments compared with hot, dry conditions. Thus, crops in hot, humid environments are likely at increased risk of  $O_3$  injury [5]. The higher enhanced risk of crops yield reduction in India because of hot and humid conditions (opened stomata) compared to hot and dry conditions (closed stomata) than cold countries in USA and Europe.

The daytime 8 h mean O<sub>3</sub> concentration between 9:00 and 17: 00 h was 40.9, 41.5, 43.2, 45.1, 46.8, 65.1, 49.1 and 22 ppbv in November, December 2006, January, February, March, April, May and June 2007, respectively. Similarly, 3 months cumulative mean O<sub>3</sub> mixing ratio was 42.2, 43.6, 45, 52.3, 53.7 and 45.4 ppbv for November 2006–January 2007, December 2006–February 2007, January–March 2007, February–April 2007, March–May 2007 and April–June 2007, respectively. AOT40 is calculated mathematically as [12]:

AOT40 = 
$$\sum_{i=1}^{n} ([O_3] - 40)_i$$
 for  $[O_3] > 40$  ppbv (1)

 $[O_3]$  = hourly averaged  $O_3$  mixing ratio in ppbv; 40 = threshold value of  $O_3$ . The 5% crop yield reduction associated with AOT40 of 3000 ppbv h (critical limit) for time period of 3 months of several crops such as wheat, onion, tomato and watermelon [13]. The AOT40 index values were calculated for different period from days after germination to harvesting of crop is shown in Table 2. It shows that throughout the period from sowing to harvesting of winter wheat and summer crop AOT40 index values were

#### Table 2

AOT40 index calculated during different months in 2006 and 2007.

Period	AOT40 (ppbv h)
November 2006 to January 2007	3575
December 2006 to February 2007	3627
January 2007 to March 2007	3745
February 2007 to April 2007	7370
March 2007 to May 2007	9150
April 2007 to June 2007	7970

higher than the critical limit value. AOT40 index was increases from November-January to March-May as O<sub>3</sub> mixing ratio start increase from October and reaches highest in April. It is seen from Table 2 that wheat crop sown in December and harvested in March reduces the yield by greater than 5% (less crop loss) associated with 3745 AOT40 index. While, wheat sown in January and harvested in April reduces the crop yield greater than 10% (more crop loss) associated with 7370 AOT40 index indicating early sowing in November-December of wheat crop is beneficial for better yield as AOT40 was low. The O<sub>3</sub> mixing ratio was at peak in April resulting highest 9150 AOT40 index from March to May which reduces maximum summer crop yields by greater than 15%. Mills et al. [13] reported that crop yield decreases linearly with increase of AOT40 index value. The O3 concentration deceases from May onwards resulting low AOT40 index 7970 due to cloudy weather condition [24]. The AOT40 values are less than critical limit from June to October on the occurrence of SW monsoon over the Indian region sparing the crop (mainly pulses and rice) loss by  $O_3$  damage.

The O<sub>3</sub> mixing ratio was low about 41–43 ppbv resulting low AOT40 values during the November-January a vegetative stage of wheat and reaches highest 45-47 ppbv resulted in high AOT40 values during reproductive and grain setting and filling phase in February-March. During the 4 months growing and harvesting period of wheat, maximum variations were found with mean O<sub>3</sub> mixing ratio, which increased from 41 ppbv in November when temperature and solar intensity were low to 65 ppbv in April when ISR and temperature were high. Debaje and Kakade [24] reported that higher mixing ratio of O<sub>3</sub> in April than in November at 3 rural sites around Ahmednagar. In the present study mean O<sub>3</sub> mixing ratio was 45 ppbv in February during the anthesis period of wheat. This period is the most important for O<sub>3</sub> effects on grain yield in cereals [10]. Considering the highest 10% wheat yield reduction occurred at seasonal mean (December-March) mixing ratio of 44.2 ppbv in the present study. Yield reductions recorded in the present study are lower than observations made by Wahid et al. [33]. Wahid et al. [33] recorded reductions of 43%, 39% and 18% in seed weight plant<sup>-1</sup> of Pasban 90, Punjab 96, and Inqilab 91 varieties of wheat, respectively at seasonal mean O<sub>3</sub> mixing ratio of 70 ppbv in Lahore, Pakistan. The nearly same reductions in crop vield in the present study when compared with studies conducted in Europe [31,32]. Pleijel et al. [32] reported yield reduction of 13% in wheat at 7 h mean mixing ratio of 42 and 44 ppbv O<sub>3</sub> during two seasons in Sweden. In India, Rai et al. [14] reported winter wheat yield decreased by 21% for O<sub>3</sub> mixing ratio of 42 ppbv at Varanasi which is twice as compared to wheat yield decrease in the present study. These difference arises in two studies was due to different methods are used to estimate the crop loss by O<sub>3</sub> pollution. Rai et al. [14] used the open-top chambers (OTC) and AOT40 index in the present study. Chameides et al. [34] estimated winter wheat loss greater than 10% due to high O<sub>3</sub> levels (>60 ppbv) in southern China using an atmospheric chemistry model along with a regional climate model similar to winter wheat loss in the present study. Wang and Mauzerall [35] explored the effect of  $O_3$  on crop yields in 2020 for China, Japan, and South Korea and showed an 82% cost increase over 1990 for China. They concluded that present day O<sub>3</sub> causes substantial crops (soybean and spring wheat) losses in this region and that significant additional losses may be expected in the order of 30% yield loss by 2020. Van Dingenen et al. [36] estimated global crop yield losses (year 2000) caused by O<sub>3</sub> for wheat range between 7% and 12%, between 6% and 16% for soybean, between 3% and 4% for rice, and between 3% and 5% for maize. They further estimate that economic losses are highest 22% for India due to crop production loss due to O<sub>3</sub> damage followed by China 21% in a global economic loss for the year 2000. The computed AOT40 values in the present study at Ahmednagar are in good agreement with model computed AOT40 values over the Indian region by Mittal et al. [11] and Engardt [12]. The small scale individual studies indicate that Asian cultivars for winter wheat and rice are equally or more sensitive to O<sub>3</sub> damage than the US cultivars [37]. The  $NO_x$  is increasing at the rate of greater than 6% year<sup>-1</sup> in the Asian countries, while maximum growth is expected to occur in India and China [25]. Lelieveld et al. [38] reported during Indian Ocean Experiment 1999 that Indian environment is strongly NO<sub>x</sub>-limited in which O<sub>3</sub> increases with increase of NO<sub>x</sub> mixing ratio indicating  $O_3$  mixing ratio will increase in near future. The increase in  $O_3$ results in increase of AOT40 index value which causes more crop yield loss. The increased emission of air pollutants in general O<sub>3</sub> precursors and elevated level of O<sub>3</sub> has become an issue of concern because of huge economic losses and threat to food security over the developing countries in particular over the Indian subcontinent.

#### 5. Conclusions

Measurements of  $O_3$  during 2006–2007 at Ahmednagar rural site clearly revealed that the magnitude of diurnal variation of  $O_3$ mixing ratio was highest in April during summer season due to intense incoming solar radiation and high temperature. The lowest of  $O_3$  was observed during SW monsoon because of more number of rainy and cloudy days. The 3-month AOT40 values are more than twice the critical limit reducing winter wheat crop yield by greater than 10% and critical limit more than thrice in summer reducing crop yield greater than 15% due to  $O_3$  damage. The Indian environments condition is favorable (hot and humid) for posing higher risk of crop loss by  $O_3$  damage as stomatal conductance is higher than in hot and dry countries. This study suggests that ambient  $O_3$ pollution in areas of Ahmednagar has potential negative impact on winter wheat and summer crop growth and yield.

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