Measurements of ozone and its precursor nitrogen dioxide and crop yield losses due to cumulative ozone exposures over 40 ppb (AOT40) in rural coastal southern India

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Abstract Measurements of ground level ozone (O₃), nitrogen dioxide (NO₂) and meteorological parameters (air temperature, relative humidity and wind speed and direction) has been made for 3 years from March 2007 to February 2010 at Nagercoil (8.2°N, 77.5°E, 23 m above sea level), an equatorial rural coastal site of southern India. The monthly average of daytime maximum of O₃ concentrations ranged from 28 to 50 parts per billion (ppb) with an annual average of 19.8 ppb. Similarly, monthly average of NO₂ concentration ranged from 3.4 ppb to 7.7 ppb with an annual average of 5.3 ppb. The monthly variation of meteorological parameters shows the little changes being a coastal site. The estimated summer crops yield losses by 1.1–15.6 % from present O₃ concentration level associated with AOT40 index 3.1–5 ppm h.

Keywords Ground level ozone · Precursor · Atmospheric conditions · Crop damage

1 Introduction

Ground level ozone (O₃) is increasing at the rate of 0.5–2 % year⁻¹ over the Northern Hemisphere due to increase in anthropogenic activities on the earth surface (Vingarzan 2004). The O₃ on which attention has becoming increasingly focused in the context of its negative impacts on human and vegetation (Ashmore et al. 2006; Amann et al. 2008). Amann et al. (2008) reported that exposure to high O₃ levels greater than 90 parts per billion (ppb) (permissible limit) hourly averages is linked to respiratory problems. Similarly, due to phytotoxic nature of O₃ greater than 40 ppb (threshold limit) has the potential to cause adverse impacts on growth and yield of agriculture and horticulture crops (Fuhrer 2009 and references
Further, $O_3$ has undesirable effects on yield quality of crops that directly affect seed and fruit chemistry as well as forage nutritive value (Royal Society 2008; Bookner et al. 2009).

$O_3$ is the most important oxidant in the troposphere. It is formed through the photochemical oxidation of precursor pollutants such as nitrogen oxides ($NO_x=NO+NO_2$), volatile organic compounds (VOC), methane ($CH_4$) and carbon monoxide (CO) in the presence of sunlight. The formation $O_3$ is controlled by $NO_x$ in India indicates that the $O_3$ concentration increases with increase of $NO_x$ concentration (Lelieveld et al. 2001). The $O_3$ precursor gases emission are mainly increasing due to increase of automobile sector. Streets et al. (2003) reported that the emission of $NO_x$ is increasing at the rate of 6.5 % year$^{-1}$ over the Indian region. The automobile contributes highest 34 % of the total $NO_x$ emission (4.6 Tg) in India between year 2000. Similarly, Ohara et al. (2007) reported that the $NO_x$ Asian emissions increased by 3 times in the year 1980–2003 with highest increase in China followed by in India. The information on $O_3$ measurements is limited in India; the available studies have suggested that $O_3$ concentrations can reach potentially damaging levels of crops (Mittal et al. 2007; Engardt 2008; Debaje et al. 2010). Model studies by Mittal et al. (2007) and Engardt (2008) have shown that the daytime monthly mean of $O_3$ concentration ranges between 30 ppb and 45 ppb for the year 2000 over the Indian region and exceeds AOT40 index critical limit of 3 ppm h of 3-months growing period of agriculture crops responsible for 5 % crops yield losses by $O_3$ damage. Further, Debaje et al. (2010) estimated that the winter wheat and summer crops yield losses by 10 % and 15 %, respectively using AOT40 index from present measured $O_3$ pollution level in the rural India.

Emberson et al. (2009) reported that crops respond differently to $O_3$ exposure in Asia (India in particular) than in USA and Europe underestimating crop yield losses occur at the present $O_3$ concentration. A recent synthesis of experimental data from Asia shows that today’s concentrations (40–80 ppb) of $O_3$ cause yield losses of three staple Asian crops (wheat, rice and legumes) that vary between 5 % and 48 %, 3–47 % and 10–65 % respectively. Similarly, Feng and Kobayashi (2009) reported wheat yield losses by 9.7 % at $O_3$ concentration 31–50 ppb using meta-analysis study and 5 % yield losses in number of crops. Wang and Mauzerall (2004) calculated that in China, Japan and South Korea 1–9 % of wheat, rice and corn yields and 23–27 % of soybean yield were lost due to 1990 levels of $O_3$ and that losses may exceed 30 % by 2020 using MOZART-2 model simulation. Van Dingenen et al. (2009) estimate economic loss for four crops (wheat, rice, maize and soybean) for the world and largest losses are found in India between US$3 and US$6 billion for the year 2000 and ranking highest economic losses about 22 % (US$ 4.5 billion) followed by 21 % (US$ 4.3 billion) in China.

A few scattered $O_3$ measurements are available over the Indian southern coastal region (Nair et al. 2002; Debaje et al. 2003; David and Nair 2011; Nishanth et al. 2012). The daytime maximum of $O_3$ concentration reaches greater than 48 ppb during the summer season at Thumba (Trivandrum) and Kannur sites (Nair et al. 2002; David and Nair 2011; Nishanth et al. 2012). Similarly, the average maximum $O_3$ concentrations greater than 40 ppb at Tranquebar was reported by Debaje et al. (2003).

In this study, we present ground level ozone ($O_3$), nitrogen dioxide ($NO_2$) and meteorological parameters (air temperature, relative humidity and wind speed and direction) measured for 3 years from March 2007 to February 2010 (study period) for the first time in this region at Nagercoil, an equatorial rural coastal site on the Arabian Sea and Bay of Bengal, a southern extreme continental part of India. Diurnal, monthly and seasonal variations of $O_3$ were studied in the light of $NO_2$ temperature, relative humidity, wind speed and direction and prevailing atmospheric conditions. The crops yield losses estimated in summer season due to cumulative $O_3$ exposures over 40 ppb using AOT40 index is discussed.
2 Location of site, measurement techniques and method

2.1 Description of site

Figure 1 presents a map of India showing measuring site-Nagercoil (8.2°N, 77.5°E, 23 m above sea level), and a few other sites which are located around it and mentioned in the present study. The population of the Nagercoil town was around 0.35 million as per 2011 census. There is no industrial complex located in the town. However, registered vehicles about 0.25 million in district Kanyakumari, Tamil Nadu state as on 1 April 2010 (STA 2010).

2.2 General meteorology

The month April is the representative for the summer season (March-May). The bright sunshine hours are experiences during these 3 months. The sunshine duration was longer (12.74 h/day)
during April and shorter (5.74 h/day) during November (CGWB 2008). Table 1 shows the atmospheric conditions observed during the study period at Nagercoil. The average highest maximum (minimum) temperature 31.5 °C (26.4 °C) in April, and lowest 30 °C (24.3 °C) was in January during winter season indicating less variation in temperature being a coastal site. The hot and cloudy weather with moderate rainfall prevails during pre-monsoon season (June–September). Nagercoil receives rainfall both from northeast (NE) monsoon (October–December) and southwest (SW) monsoon (June–September); however, it seems that NE monsoon is more active than the SW monsoon. The month November is a rainiest month during NE monsoon season. The total annual normal rainfall is 83 cm reported by the nearest observatory Kanyakumari (8.1°N, 77.5°E, 37 m above sea level), India Meteorological Department (IMD) (http://www.imd.gov.in). Fair weather conditions prevail in the month of February is the representative for the winter season (January–February). The surface meteorological parameters such as cloud cover and rainfall are used from Kanyakumari observatory to explore their role on O3 formation (Debaje et al. 2003; IMD 2010).

2.3 Measurement techniques

Measurement of O3, NO2 in parts per billion (ppb) and meteorological parameters were carried out using the Aeroqual Series 200 Handheld Monitor (Aeroqual Limited, New Zealand) at Nagercoil, India. The more details about the instrument are available at website www.aeroqual.com. Gas Sensitive Semiconductor (GSS) technology is used to measured the gases. The sensor head is controlled by intelligent data logger. The operating chemical parameters are O3 (detection range 0–500 ppb) and NO2 (detection range 0–200 ppb). The lower detection limit for O3 and NO2 is 1 ppbv and response time for O3 less than 70 s and NO2 less than 60 s. The meteorological parameters such as air temperature (°C), relative humidity (%) and wind speed (ms−1) and direction (16 points compass) are also measured using different sensors. The lower detection limit for temperature sensor is 0.01 °C and for relative humidity sensor 1 % and response time less than 1 s. All times are given in Indian Standard Time (IST), which is ahead of the GMT by 05:30 h. The O3 sensor was calibrated with the ultraviolet (UV) photometric O3 analyzer (Model: O342M, Environmental S. A., France) by running them together with averaging time interval of 1 h, and correlation coefficient is found to be 0.86–0.94. Similarly, NO2 sensor was calibrated with the chemiluminescence’s technique (Model: APNA 365 analyzer, Horiba, Japan) by running them together with averaging time interval of 1 h, and correlation coefficient is 0.84–0.91.

All data analyses in this study are based upon the hourly averaged of O3, NO2, temperature, relative humidity and wind speed and direction. The daily means of O3, NO2, temperature, relative humidity and wind speed and direction was calculated from the hourly average. The monthly average of O3, NO2, temperature, relative humidity and wind speed and direction was calculated from the daily mean for each month. The monthly average daytime maximum value of O3 was calculated from averaging daily single maximum values of O3 concentration for each month. The monthly diurnal means of O3, NO2, temperature and relative humidity was computed by averaging for all days of a month for specific hour. The annual and seasonal diurnal means of O3 are computed by averaging for all months of a year.

2.4 Method

Crop yield losses due to cumulative O3 exposures over 40 ppb was estimated using AOT40 index (accumulated O3 concentration over a threshold of 40 ppb) (Mills et al. 2007). AOT40 is the hourly mean O3 concentration accumulated over a threshold O3 concentration of
Table 1  Monthly variation of air temperature (minimum/maximum), relative humidity (minimum/maximum) and wind speed and direction measured for 3 years from March 2007 to February 2010 at Nagercoil

|                | Air temperature (°C) | Relative humidity (%) | Wind speed (ms⁻¹)/Direction |
|----------------|-----------------------|-----------------------|----------------------------|
|                | 2007–08   | 2008–09   | 2009–10  | Avg. | 2007–08   | 2008–09   | 2009–10  | Avg. | 2007–08 | 2008–09 | 2009–10 |
| March          | 25.3/31.1 | 25.4/30.4 | 26.6/31.3 | 25.6/30.9 | 59/81 | 55/77 | 60/79 | 58/79 | 1.9/W | 1.9/WSW | 1.7/W |
| April          | 26/31.8   | 26.6/31.2 | 27.3/31.7 | 26.4/31.5 | 61/83 | 59/79 | 58/79 | 59/80 | 2/W | 1.8/WNW | 2.3/W |
| May            | 26.7/31.4 | 26.8/31.1 | 27.5/30.9 | 27/31.1 | 65/86 | 63/82 | 64/80 | 64/83 | 2.2/NW | 2/WNW | 2/WNW |
| June           | 24.4/29.5 | 25.8/30   | 26.3/30   | 25.5/29.8 | 72/89 | 70/88 | 73/86 | 72/88 | 1.5/NW | 2.2/WNW | 2.2/WNW |
| July           | 24.4/28.9 | 25.2/29.4 | 25.4/29.7 | 25.9/29.3 | 75/90 | 75/91 | 76/90 | 75/90 | 2.5/WNW | 2.6/NW | 3/NW |
| August         | 25.5/29.5 | 25.1/29.8 | 25.4/29.8 | 25.3/29.7 | 70/87 | 74/88 | 74/90 | 73/88 | 2.7/NW | 2.6/WNW | 2.6/NW |
| September      | 24.8/29.1 | 25.3/29.5 | 25.9/29.6 | 25.3/29.4 | 71/91 | 72/88 | 75/89 | 73/89 | 2.2/NW | 2.2/NW | 2.3/WNW |
| October        | 25.9/29.7 | 25.4/29.6 | 26.0/29.8 | 25.7/29.7 | 68/89 | 71/88 | 71/85 | 70/87 | 1.6/W | 1.9/W | 2.9/WNW |
| November       | 24/30.3   | 25.6/29.9 | 25.5/29.5 | 25/29.9 | 64/91 | 69/92 | 72/92 | 68/92 | 1.5/N | 1.7/NE | 1.6/NE |
| December       | 25/30.5   | 24.7/30.4 | 25.7/29.8 | 25.1/30.2 | 63/83 | 65/87 | 63/84 | 64/85 | 1.3/W | 2.3/SW | 1.4/SW |
| January        | 24.5/30.7 | 23.6/29.8 | 24.8/29.6 | 24.3/30  | 52/80 | 56/81 | 62/80 | 57/80 | 1.6/WSW | 1.2/SW | 1.5/WSW |
| February       | 24.3/30.9 | 24.7/29.9 | 25.9/30.9 | 24.9/30.5 | 54/79 | 56/81 | 55/76 | 55/79 | 2/W | 1.5/W | 1.3/W |
| Avg.           | 25.2/30.2 | 25.4/30.2 | 25.8/30.2 | 25.4/30.2 | 65/86 | 66/85 | 66/84 | 66/85 | 2/W | 1.5/W | 1.3/W |
40 ppb during daylight hours for 3-months of growing (November-December) to harvesting (March–April) period for agricultural and horticulture crops and is linearly correlated with crop yield reduction, unit’s parts per million hours (ppm h, hourly average). AOT40 is calculated mathematically as (Engardt 2008):

\[
\text{AOT}_{40} = \sum_{i=1}^{n} \left( [O_3] - 40 \right)_i \text{ for } [O_3] > 40 \text{ ppb during daylight hours}
\]

\([O_3] = \) hourly averaged O3 concentration in ppb; 40 = threshold limit of O3 and n is the number of hours from growing to harvesting season of crop.

3 Results and discussion

3.1 Diurnal variation

Figure 2a shows the annual average diurnal variations of O3 for the 3 years 2007, 2008 and 2009. The highest and lowest concentration of O3 was observed in April and November, respectively; hence, it is investigated separately in Fig. 2b. The annual average daytime maximum of O3 concentration 33.3±8, 30.3±8 and 34.6±10 ppb in the afternoon around 15:00 h and minimum of O3 9.1±5, 9±5 and 9.8±7 ppb at the sunrise 06:00 h with 1σ standard deviation in 2007, 2008 and 2009, respectively (Fig 2a). The highest maximum of O3 concentration 49.7±17 ppb (27.7±8 ppb) (average for 3 years) was observed in the afternoon and minimum of O3 16.5±11 ppb (8.1±6 ppb) at the sunrise in April (November) (Fig. 2b). It was observed that hourly averaged daytime highest maximum of O3 exceeds 75 ppb in the afternoon in April attributed to the high temperature and clear sky along with high NO2 concentration (favorable conditions for O3 formation).

The daytime maximum of O3 concentration was observed between 14:00 h and 16:00 h, and corresponding maximum air temperature attained between 13:00 h and 15:00 h indicating peak O3 concentration lagged behind nearly by 1–2 h from peak air temperature (Figs. 2 and 4). Debaje and Kakade (2009) reported the similar time lag from peak air temperature to peak O3 concentration at continental rural site. Similarly, the maxima of O3 concentration were always observed in the afternoon in all seasons similar to other coastal rural sites in southern India, a characteristic of rural site (Nair et al. 2002; Debaje et al. 2003; David and Nair 2011; Nishanth et al. 2012).

Figure 3a, b shows the annual average diurnal variation of NO2 for 3 years 2007, 2008 and 2009, and diurnal variation in April and November. It is seen from the Fig. 3a that highest NO2 concentration 6.5, 6.5 and 6.6 ppb was observed at around midnight 24:00 h and minimum of NO2 1.7, 1.8 and 2.8 ppb in the afternoon at 15:00 h in 2007, 2008 and 2009, respectively. The maximum of O3 concentration formed at around 15:00 h, and corresponding minimum of NO2 observed at the same time indicate that NO2 utilized in the O3 formation. The significant year to year differences in annual diurnal NO2 variation were not observed in 3 years period, however, higher NO2 concentration was observed in 2009 than NO2 concentration in 2007 and 2008. The maximum NO2 concentration 8.5 ppb (4.2 ppb) was observed in the midnight and the minimum of NO2 3.2 ppb (0.9 ppb) in the afternoon in April (November) (Fig. 3b). It is to be noted that the small upper side kink in the diurnal pattern of NO2 were observed at around 9:00 h due to morning rush hours of traffic emission.

The high concentration of NO2 in April was due to biomass burning and low NO2 in November because of rainy season. The biomass burning from March to May in India results
in emission of NO\textsubscript{x} and VOC lead to more photochemical buildup of O\textsubscript{3} in rural areas (Galanter et al. 2000). Further, the emissions of biogenic hydrocarbons (e.g. isoprene) increases with increase of temperature help produce more O\textsubscript{3} in summer season (Velasco 2003). Similarly, Figs. 4a, b and 5a, b show the annual average diurnal variation of temperature and relative humidity, respectively, and diurnal variation in April and November. The annual maximum temperature around 30.1 °C, 30.2 °C and 30.4 °C was observed in the afternoon (14:00–15:00 h) and minimum of 25.5 °C, 25.4 °C and 25.6 °C in the morning (6:00 h) in 2007, 2008 and 2009, respectively (Fig. 4a). The maximum temperature 31.7 °C (29.8 °C) was observed in the afternoon around 15:00 h and minimum of 27.3 °C (25.5 °C) in the morning 6:00 h in April (November) (Fig. 4b). The highest temperature greater than 36 °C were also observed on clear sky days in April, related to highest O\textsubscript{3} formation. The highest relative humidity was observed in November and lowest in April, related to lowest O\textsubscript{3} concentration in November because photochemical formation of O\textsubscript{3} decreases with increase of relative humidity and overcast sky (unfavorable conditions for O\textsubscript{3} formation) (Debaje et al. 2003). The westerly wind of the order of 2–2.3 ms\textsuperscript{-1} was in April favor for high O\textsubscript{3} concentration; while northeasterly wind 1.5-1.7 ms\textsuperscript{-1} in November decreases O\textsubscript{3} concentration (Table 1).
3.2 Seasonal variation

Table 2 shows the comparison of monthly average O₃ concentration at Nagercoil and other nearby coastal sites O₃ measured available in India. The monthly average of NO₂ measured also shown in Table 2. The highest average of O₃ concentration in the range 24.9–27.9 ppb was observed in April. The corresponding average highest NO₂ concentration 6.8 ppb was in April indicating that O₃ increases with increase of NO₂. The lowest O₃ concentration 14.4–16.9 ppb was observed in November and corresponding lowest NO₂ concentration about 4 ppb indicate that the O₃ decreases with decrease of NO₂ concentration. The annual averaged O₃ concentration was 19.8 ppb for the study period with highest annual O₃ concentration 20.6 ppb in 2009 followed by 19.7 ppb and 19.2 ppb in 2007 and 2008, respectively. The rate of increase of O₃ is 2.4 % year⁻¹ for the study period, which is higher than the O₃ increase rate 1.45 year⁻¹ during 1954–55 and 1991–93 in Ahmedabad, India reported by Naja and Lal (1996).

Similarly, annual averaged NO₂ concentration 5.3 ppb was for 3 years period with highest annual NO₂ concentration 5.8 ppb in 2009. The higher annual average O₃ concentration in 2009 than in 2007 (4.6 ppb) and 2008 (5.6 ppb) was due to the higher NO₂ concentration in 2009. The rate of increase of NO₂ is 8.6 % year⁻¹ for the study period, which is also higher
than the rate of increase of NO\textsubscript{x} 6.5 % year\textsuperscript{−1} in India between 2000 reported by Streets et al. (2003). The O\textsubscript{3} concentrations linearly depend on emission of NO\textsubscript{x} in the rural sites (Wang et al. 2001). It is seen from the Table 2 that O\textsubscript{3} measured at Nagercoil is in good agreement on seasonal basis with O\textsubscript{3} measured at Thumba. Similarly, O\textsubscript{3} measured at Nagercoil are in good agreement with the O\textsubscript{3} measured in April and in November at Tranquebar and Kannur.

4 Crop exposure to O\textsubscript{3}

The monthly average daytime maximum of O\textsubscript{3} concentration was 37.8, 42.1, 45.4, 43 and 40.2 ppb in February, March, April, May and June in 2007, respectively. The 3-months cumulative mean O\textsubscript{3} concentration was 41.8, 43.5 and 42.9 ppb for February–April, March–May and April–June 2007. Similarly, monthly daytime maximum O\textsubscript{3} concentration 39, 40.3, 43.9, 41.7 and 40.2 ppb in February, March, April, May and June in 2008, respectively. The 3-months cumulative mean O\textsubscript{3} concentration was 41, 42 and 41.9 ppbv for February–April, March–May and April–June 2008, respectively. The monthly daytime maximum O\textsubscript{3} concentration 38.4, 42.2, 59.3, 46.5 and 39.5 ppb in February, March, April, May and June in 2009, respectively. The 3-months cumulative mean O\textsubscript{3} concentration was 46.6, 49.3 and 48.4 ppb for
February–April, March–May and April–June 2009, respectively indicating crop yield losses due to O₃ exposure. The daytime hourly averaged O₃ concentration less than threshold limits of 40 ppb was observed from July to January each year for 2007, 2008 and 2009.

4.1 AOT40 index

The monthly AOT40 index value was calculated using Equation (1) from February to June in 2007, 2008 and 2009. Further, cumulative 3-months AOT40 value was calculated for different period such as February–April, March–May and April–June. Table 3 shows the summary of calculated AOT40 index values for the different period. The highest AOT40 index value was 3.1 ppm h, 2.6 ppm h and 5 ppm h in March–May 2007, March–May 2008 and March–May 2009, respectively used for estimation of crop yield losses due to O₃ damage. The AOT40 critical limits for 5 % crop yield losses for O₃ sensitive crops (watermelon, pulses (black gram (urd) and red gram (tur), green gram (moong)), cotton, wheat, onion, tomato) and moderately sensitive crops (oilseeds (groundnut, caster), potato, rice and maize) are used from Mills et al. (2007). The different AOT40 critical limits for 5 % crops losses for different crops: watermelon, pulses, cotton, wheat, onion, tomato, oilseeds,
Table 2  Monthly average ground level ozone (O₃) and nitrogen dioxide (NO₂) concentration (ppb) measured at Nagercoil for 3 years from March 2007 to February 2010 and O₃ at other site measurements available over Indian nearby coastal region

|       | O₃  | NO₂  | Thumbaᵃ | Tranquebarᵇ | Kannurᶜ |
|-------|-----|------|---------|-------------|---------|
|       | 2007–08 | 2008–09 | 2009–10 | Avg. | 2007–08 | 2008–09 | 2009–10 | Avg. | 1998–99 | 1997–2000 | 2009–10 |
| March | 24.6  | 22.8  | 24.7  | 24  | 5.5 | 7.1 | 7 | 6.5 | 22 | 22.4 | 27.4 |
| April | 26.3  | 24.9  | 27.9  | 26.4 | 5.7 | 7.5 | 7.4 | 6.8 | 20.7 | 23.6 |
| May   | 22.7  | 24.5  | 26.8  | 24.7 | 5.2 | 7 | 7.7 | 6.6 | 17.4 | 22.5 | 21 |
| June  | 19.9  | 21.5  | 22  | 21.1 | 5.1 | 6.8 | 6.4 | 6.1 | 16.4 | 19.8 |
| July  | 20.6  | 19.6  | 21 | 20.4 | 4.7 | 5.8 | 6.3 | 5.6 | 15.7 | 21.1 | 15.3 |
| August | 18.7 | 17.7  | 18.9 | 21.4 | 4.6 | 5.6 | 5.5 | 5.3 | 15.9 | 13.1 |
| September | 17.4 | 16.6  | 17.6 | 17.2 | 4.3 | 5.1 | 5.2 | 4.8 | 13 | 14.5 |
| October | 16.3 | 15.6  | 14.7 | 15.5 | 3.4 | 4.4 | 4.7 | 4.1 | 15.1 | 17.5 | 16 |
| November | 14.4 | 13.9  | 16.9 | 15 | 3.8 | 4 | 4 | 3.9 | 16.5 | 20.2 |
| December | 15.8 | 16.7  | 18 | 16.8 | 3.9 | 5 | 4.8 | 4.5 | 17.8 | 25.4 |
| January | 17 | 18.4  | 19.2 | 18.2 | 4.2 | 5.1 | 5.1 | 4.8 | 20.5 | 20.7 | 31 |
| February | 19.1 | 20.2  | 19.1 | 19.9 | 4.4 | 5.6 | 5.7 | 5.3 | 21.4 | 29.7 |
| Avg. | 19.7 | 19.2  | 20.6 | 19.8 | 4.6 | 5.6 | 5.8 | 5.3 | 17.7 | 20.5 | 21.4 |

ᵃNair et al. (2002)
ᵇDebaje et al. (2003)
ᶜNishanth et al. (2012)
potato, rice and maize are 1.6, 3, 3.1, 3.3, 4.1, 6, 8.9, 8.9, 12.8 and 13.9 ppm h, respectively. Large number of varieties of agriculture and horticulture crops is grown over this area which is O₃ sensitive and moderately sensitive to O₃. In addition to the above crops, millets (bajara, ragi, jowar (sorghum, sweet sorghum), sesame, bean, jute, tea, coffee, sugarcane, mangoes, bananas, orange, grape, pepper, cardamom, chilies, cashew nut, coconut and natural rubber are also grown (http://www.tnau.ac.in/tech/acpen.pdf).

Table 4 shows the estimated crop yield losses for different crops using highest AOT40 index value in 2007, 2008 and 2009. The crops yield losses ranged from 1.1 % to 9.7 %, 0.9–8.1 % and 1.8–15.6 % in 2007, 2008 and 2009 associated with AOT40 index values 3.1 ppb h, 2.6 ppb h and 5 ppb h, respectively indicate that highest crops yield losses in 2009. The higher crop yield losses were observed for O₃ sensitive crops than for moderately sensitive crops. The crops yield losses is highest for watermelon (9.7 %), followed by pulses (5.2 %), cotton (5 %) and wheat (4.7 %) in 2007. The crops yield loss is low in 2008 compared to crops yield loss in 2007 and 2009. The highest watermelon yield losses by 15.6 %, while pulses and wheat losses by 8.3 % and 7.6 %, respectively was observed in 2009. It is seen from the above estimation that AOT40 index values exceed critical limit for 5 % yield losses of crop which are O₃ sensitive during March–May indicating that the present O₃ concentration has negative effects on crop yield due to O₃ exposure in summer season.

The stomatal conductance is higher in hot and humid environments in Asia, particularly in India poses more damage to crops due to O₃ exposure than in hot and dry environments in some

| Period                  | AOT40 (ppm h) |
|-------------------------|---------------|
| March 2007 to May 2007  | 3.1           |
| April 2007 to June 2007 | 1.8           |
| February 2008 to April 2008 | 1.2   |
| March 2008 to May 2008  | 2.6           |
| April 2008 to June 2008 | 1.4           |
| February 2009 to April 2009 | 3.5   |
| March 2009 to May 2009  | 5             |
| April 2009 to June 2009 | 2.7           |

Table 3 AOT40 index calculated during different months in 2007, 2008 and 2009

| Crops/years | 2007 | 2008 | 2009 |
|-------------|------|------|------|
| Sensitive to O₃ |      |      |      |
| Watermelon   | 9.7  | 8.1  | 15.6 |
| Pulses       | 5.2  | 4.3  | 8.3  |
| Cotton        | 5    | 4.2  | 8    |
| Wheat         | 4.7  | 4.2  | 7.6  |
| Onion         | 3.8  | 3.9  | 6.1  |
| Tomato        | 2.6  | 2.2  | 4.2  |
| Moderately sensitive to O₃ |      |      |      |
| Oilseed       | 1.7  | 1.4  | 2.8  |
| Potato        | 1.7  | 1.4  | 2.8  |
| Rice          | 1.2  | 1    | 1.9  |
| Maize         | 1.1  | 0.9  | 1.8  |
areas of Europe and USA (Fiscus et al. 2005). Further, crops sensitive to O₃ are at more risk due to likely co-occurrence of peak levels of O₃ and growing period of these crops from February to May. Winter wheat is especially sensitive to O₃ in India due to the likely co-occurrence of peak levels of O₃ and growing season (Emerson et al. 2003). The estimated crop yield losses by 1.1–15.6 % using AOT40 index due to O₃ damage at Nagercoil similar to other locations in India and Asia (Wahid 2006; Rai et al. 2007; Debeje et al. 2010). Wahid (2006) estimate reductions of 43 %, 39 % and 18 % in seed weight plant⁻¹ of Pasban 90, Punjab 96 and Inqilab 91 varieties of wheat, respectively at seasonal mean O₃ concentration of 70 ppb by experimental study in Lahore, Pakistan. Rai et al. (2007) reported winter wheat yield losses by 21 % using open top chambers study for O₃ concentration of 42 ppb at Varanasi, India.

The NO₂ is increasing at the rate of 8.6 % year⁻¹ at Nagercoil due to growth of automobiles sector, where no restrictive measures on emissions of O₃ precursors (particularly NOₓ) were assumed to be implemented. The elevated O₃ concentration in future has direct negative effects on crops yield production threatening the food security in India. We use the AOT40-yield response functions obtained in Europe to estimate crop production losses in the present study. The O₃ exposure-response relationships function not established in India due to limited experiments, hence, no alternative approach is possible. Our results suggest that future crop yield reductions due to O₃ damage will be large, if no mitigation efforts for O₃ precursor are implemented.

5 Conclusions

Measurements of O₃, NO₂, temperature, relative humidity, wind speed and direction was made during 2007–2010 at Nagercoil, a rural coastal site in India clearly revealed that the O₃ concentration was higher in April than in November attributed to high NO₂ concentration, high temperature and low relative humidity. The monthly average of daytime maximum of O₃ concentrations ranged from 28 ppb to 50 ppb with an annual increase rate of O₃ is 2.4 %. Similarly, monthly average of NO₂ concentration ranged from 3.4 ppb to 7.7 ppb with an annual increase rate of NO₂ is 8.6 %. The estimated summer crops yield losses by 1.1–15.6 % associated with AOT40 index values 3.1–5 ppm h. This study suggests that ambient O₃ pollution in areas of Nagercoil has potential negative impact on crop growth and yield during the summer season. We feel that more such extensive observations of O₃ and its precursor are needed to understand the effect of O₃ on crop yield losses.

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