REVIEW ARTICLE

Tropospheric ozone pollution in India: effects on crop yield and product quality

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Abstract Ozone (O_3) in troposphere is the most critical secondary air pollutant, and being phytotoxic causes substantial losses to agricultural productivity. Its increasing concentration in India particularly in Indo-Gangetic plains is an issue of major concern as it is posing a threat to agriculture. In view of the issue of rising surface level of O_3 in India, the aim of this compilation is to present the past and the prevailing concentrations of O_3 and its important precursor (oxides of nitrogen) over the Indian region. The resulting magnitude of reductions in crop productivity as well as alteration in the quality of the product attributable to tropospheric O_3 has also been taken up. Studies in relation to yield measurements have been conducted predominantly in open top chambers (OTCs) and also assessed by using antiozonant ethylene diurea (EDU). There is a substantial spatial difference in O_3 distribution at different places displaying variable $O₃$ concentrations due to seasonal and geographical variations. This review further recognizes the major information lacuna and also highlights future perspectives to get the grips with rising trend of ground level O_3 pollution and also to formulate the policies to check the emissions of O_3 precursors in India.

Keywords Crop productivity \cdot Ethylene diurea \cdot India \cdot Oxides of nitrogen . Ozone . Quality . Yield

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Introduction

During the last few decades, tropospheric ozone (O_3) has become one of the widest spread toxic pollutants around the globe (IPCC [2007;](#page-12-0) Booker et al. [2009](#page-12-0)) with negative impact on humans, animals, and plants (Cho et al. [2011](#page-12-0)). Though being a toxicant at ground level, O_3 in upper troposphere plays a role in controlling the atmospheric chemistry due to its influential role in the heat balance of atmosphere leading to climate change (Khemani et al. [1995\)](#page-13-0). Ozone in upper troposphere plays a major role in greenhouse effect, as 1 Dobson unit increase in O_3 produces a temperature increase of about 0.02 K (Ahammed et al. [2006\)](#page-12-0). Being a secondary pollutant in troposphere, O_3 is formed by a chain of photochemical reactions involving its various precursors such as methane (CH_4) , carbon monoxide (CO), nitrogen oxides (NO_x) , and volatile organic compounds (VOCs) in the presence of bright sunlight (Collins et al. [1997\)](#page-12-0). Having a considerable share from industrial emissions and other anthropogenic activities, transport sector also contributes significantly to emissions of O_3 precursors leading to O_3 formation in urban areas. Apart from being a pollutant of concern in cities and metropolitans, ground level $O₃$ is also a problem in rural areas. Due to long-distance transport, though being located hundreds or thousands miles away from the original source, remote rural areas experience high concentrations of O_3 , where majority of land areas are dedicated to agricultural practices (Prather et al. [2003;](#page-14-0) Agrawal et al. [2003](#page-12-0)). Two mechanisms have been proposed for its higher levels in rural environment. Firstly, the direct transport of O_3 from urban areas, and secondly, the transport of its precursors like NO_x , VOCs, CO, CH₄, and nonmethane hydrocarbons followed by in situ photochemical $O₃$ production (Naja and Lal [2002\)](#page-13-0). Another source of O_3 in troposphere is through transport from stratosphere (Forster et al. [2007](#page-13-0)), but its contribution to O_3 built up is relatively low.

Background concentrations of ground-level O_3 has risen from an estimated preindustrial concentration of 10 ppb to average summer concentrations varying from 30 to 50 ppb in mid-latitudes of the northern hemisphere and O_3 episodes reaching 100 ppb (Morgan et al. [2006\)](#page-13-0). With current air quality legislation implemented worldwide, multimodal simulations for 2030 projected that global surface O_3 would increase by 1.5 ± 1.2 ppb on average, and for IPCC SRES A2 scenario, by 4.3 ± 2.2 ppb with the strongest increases in South Asia, Southeast Asia, and the Middle East (Gauss et al. [2007](#page-13-0)). According to Dentener et al. [\(2005\)](#page-12-0), global photochemical models project that as per the current legislation of O_3 precursor emissions; parts of Asia will experience further significant increase in O_3 concentration up to 2030. Monitoring reports of $O₃$ in suburban and rural areas of Asia also showed that mean monthly O_3 concentration now commonly reach up to 50 ppb (EANET [2006](#page-12-0)).

Ozone gains entry inside the leaves through stomatal pores. Upon reaching the intercellular spaces, it rapidly generates reactive oxygen species (ROS) and also reacts with components of the leaf apoplast causing oxidative stress (Booker et al. [2009\)](#page-12-0). As a result, antioxidant defense system is triggered which plays a decisive role of keeping ROS levels under control, thereby maintaining cellular redox balance. Thus, un $der O₃ stress, induced metabolic pathways, reduction in pho$ tosynthetic proteins, impaired reproductive development and accelerated senescence conclusively leads to decreased carbon assimilation and alterations in its partitioning resulting in lower accumulation of biomass in plants (McCrady and Andersen [2000\)](#page-13-0), reductions in yield and modification in crop quality (Black et al. [2000;](#page-12-0) Singh et al. [2009a](#page-14-0); Tripathi and Agrawal [2012;](#page-15-0) Sarkar et al. [2015\)](#page-14-0). Previously, several studies have reported reduction in crop yield due to O_3 (Feng et al. [2009](#page-13-0); Feng and Kobayashi [2009;](#page-13-0) Sawada and Kohno [2009;](#page-14-0) Rai et al. [2010;](#page-14-0) Sarkar and Agrawal [2010](#page-14-0); Mishra et al. [2013](#page-13-0); Singh et al. [2014](#page-14-0)). The relative regional yield loss in developing countries of East Asia (India, Pakistan, and Bangladesh) in year 2000 was 8–27% for wheat, 3–13% for soybean, and 3– 8% for maize based on the M12 or AOT40 metrics used for O_3 exposure (Avnery et al. [2011\)](#page-12-0). Van Dingenen et al. [\(2009\)](#page-15-0) calculated that in the year 2000, an economic loss of nearly US\$6.3–12.0 billion took place globally for four major crops (wheat, rice, maize, and soybean) out of which India and China shared 22 and 21%, respectively, of the total damage. Studies conducted at global level in relation to $O₃$ induced crop yield losses has also shown that relative yield loss (RYL) leading to economic cost losses (ECL) are highest in India followed by China (Van Dingenen et al. [2009;](#page-15-0) Avnery et al. [2011](#page-12-0)). Takigawa et al. ([2009](#page-14-0)), in their global regional CTM-based analysis, estimated that yield reduction due to $O₃$ in spring wheat will increase by 7.4 and 7.7% in China and India, respectively, by the year 2020 as compared to 2002. A model-based study suggested that yield losses of 5–20% for important crops may be common in areas experiencing higher $O₃$ concentrations and concluded that Asian grown wheat and rice cultivars are more sensitive to O_3 than the cultivars of North America (Emberson et al. [2009\)](#page-12-0).

India is one of the rapidly growing economies in the Asian region and large emissions from industries, automobiles, other anthropogenic activities and relatively high solar intensity provide most favorable conditions for the formation of surface O3. Due to anthropogenic emissions, several chemical transport models have estimated large increases in $O₃$ production over the Indian region (Berntsen et al. [1996](#page-12-0); Brasseur et al. [1998;](#page-12-0) Oksanen et al. [2013\)](#page-13-0). India is an agriculture-based economy, and its 58% of the population relies on agriculture for livelihood. Agriculture in India is demographically the broadest economic sector, ranking worldwide second in its farm production (Ghude et al. [2014](#page-13-0)). Nearly 1.2 billion people of India depend largely on food produced within the country, and simultaneously, other African and Asian nations depend mostly on import of Indian rice (Burney and Ramanathan [2014\)](#page-12-0). Since the yield losses caused due to O_3 pose a greater risk to food supply, the increasing O_3 pollution is one of the major threats for agriculture sector in India, being the home of one fifth hungry population of the world. According to the estimations of Van Dingenen et al. [\(2009\)](#page-15-0), economic losses of four crops (wheat, rice, maize and soybean) were found to be largest in India ranging between US\$3 to US\$6 billion for the year 2000. According to different monitoring reports, throughout India, there is higher incidence of $O₃$ formation in the areas falling under agriculture production.

Thus, the aim of this compilation is to highlight the prevalence of O_3 and its concentrations over different locations of India and resulting magnitude of reductions in crop productivity as well as alterations in the quality of their product collated from the literature published. The present review could be beneficial in (a) adding knowledge about the prevailing O_3 concentrations in India and its direct correlation with the economic consequences of agriculture production losses that might be critical for food security, (b) to make and implement long-term policies to curb the emissions of O_3 precursors, and (c) to set standards in relation to O_3 for agriculture in India.

NO_x concentration in Indian region: a potent $O₃$ precursor

Microclimatic conditions and availability of O_3 precursors are the two prime factors responsible for O_3 formation. One of the most prominent O_3 precursors contributing to O_3 formation is oxides of nitrogen (NO_x) . NO_x includes chiefly nitric oxide (NO) and nitrogen dioxide (NO₂). According to EPA [\(2007\)](#page-13-0), tropospheric O_3 is formed by a series of reactions involving volatile organic compounds (VOCs) combined with NO_x in the presence of sunlight. NO_x molecules participate in competing O_3 creation and destruction reactions (Simon et al. [2014\)](#page-14-0). A wavelength of 430 nm of sunlight breaks $NO₂$ into NO and O. The free oxygen atom then combines with oxygen molecule to form tropospheric O_3 . VOCs play a prominent role in process by which "free radicals" convert NO into $NO₂$ and $NO₂$ then breaks again into NO and O leading to the continuation of this cycle (Ghazali et al. [2010\)](#page-13-0). At low NO_x concentrations, $O₃$ production is limited by the availability of NO_x molecules, while at high NO_x concentrations, availability of other compounds limits O_3 production (Lin et al. [1988](#page-13-0)).

 NO_x emissions have been increasing over Indian region due to rapid economic growth, uncontrolled use of fossil fuels in industries and extended transport sector. Records of ministry of surface transport in India had tabulated that the number of vehicles in the country was 21.3, 53, and 67 million in 1991, 2000, and 2003, respectively (Rai et al. [2011a\)](#page-14-0), which has now been increased up to 159.4 million in 2012 (https://data.gov.in/catalog/total-number-registered-motorvehicles). Lelieveld et al. ([2001](#page-13-0)) reported that the formation of O_3 in India is predominantly controlled by NO_x , indicating a positive correlation between O_3 and NO_x concentration. Model studies have confirmed that the growing NO_x emissions in India account for the consistent increase in background $O₃$ levels over the past three decades (Horaginamani and Ravichandran [2010\)](#page-13-0). Annual average $NO₂$ levels across India for the year 2007 depicted that the maximum emissions of NOx were prevalent in north-eastern and west-eastern parts of India (Oksanen et al. [2013](#page-13-0)).

According to Garg et al. ([2001](#page-13-0)), NO_x emissions over the Indian region were growing at an annual rate of 5.5% year⁻¹, while Streets et al. ([2003\)](#page-14-0) found an increase rate of 6.5% year−¹ , displaying an increasing trend. Beig and Brasseur [\(2006\)](#page-12-0) showed that maximum increase of NO_x concentration from 1991 to 2001 was about 0.5–1.5 ppb (20– 50%). Air quality monitoring conducted by the Indian government organization Central Pollution Control Board (CPCB) in various cities had shown a dramatic increase in NO_x concentrations since 1990. For the year 2009, it has been reported that prevalence of NO_x concentrations was 4.3 to 42.9 ppb in various parts of the country with peak concentrations in metropolitan cities (Rai and Agrawal [2012](#page-14-0)). Lu and Streets ([2012\)](#page-13-0) found an increase of 70% in NO_x emissions from 1996 to 2010 from Indian public thermal power plants.

Lal et al. ([2000\)](#page-13-0) found that the diurnal and seasonal variations at Ahmadabad were affected by mutual effects of local emissions, boundary layer processes, and wind pattern. Horaginamani and Ravichandran [\(2010\)](#page-13-0) monitored oxides of nitrogen in ambient air from August 2008 to January 2009 (24 h) at eight different sampling stations in Tiruchirappalli (Table [1\)](#page-3-0). The concentrations ranged from 67.4 to 90.2 ppb exceeding the quality standards of CPCB at all sampling stations except at one site. Increasing concentrations of NO_x were also modeled by van der et al. [\(2008\)](#page-15-0) and Ghude et al. [\(2008\)](#page-13-0) showing an annual growth of 7.4 and 2.4% in Delhi and a larger region of North India, respectively, chiefly due to industrial growth and vehicular traffic load. Indo-Gangetic Plain (IGP) region is highly vulnerable to human induced pollutant emissions due to its conductive weather pattern. Beig and Ali ([2006](#page-12-0)) used Model for Ozone Related Tracers (MOZART) which revealed maximum value of 7.5 ppb and minimum value of 0.4 ppbv over IGP while the distribution of NO_x over rest of the Indian landmass was in the range of 1.6– 4.0 ppb (Beig and Ali [2006](#page-12-0)). Annual mean concentration of NO2 ranged from 10.1 to 31.3 ppb in different zones of Varanasi city in 1990, while it varied from 16 to 155 ppb during 1999–2001 (Trivedi and Agrawal [2003](#page-15-0); Rai and Agrawal [2012](#page-14-0)). Concentrations of $NO_x/NO₂$ in different cities of India are given in Table [1.](#page-3-0)

Ozone concentration in different regions of India

Being located in subtropical region, Indian subcontinent encounters fairly high O_3 concentrations. Representative O_3 concentrations at different monitoring stations in India are shown in Fig. [1](#page-3-0). Global chemical transport models suggested that surface O_3 concentration could increase to a level 25– 30 ppb in tropical India between years 2000 and 2100 (Prather et al. [2003\)](#page-14-0). Debaje and Kakade [\(2009\)](#page-12-0) monitored surface O_3 variability for the period 2001–2005 over western Maharashtra taking up five different sites. Seasonal variation of O_3 displayed a maximum concentration of 40–50 ppb in summer and winter season at the urban sites, and similar levels were observed at rural site in spite of less emission of precursors. While at a high altitude mountain site, comparatively less O3 formation (30–40 ppb) was observed (Debaje and Kakade [2009\)](#page-12-0). Monthly AOT40 as high as 36 ppmh were found between November to April 2003 over Pune (Roy et al. [2009\)](#page-14-0). According to Tiwari and Peshin ([1995](#page-14-0)), surface O_3 concentration at Pune during 1988–1991 had increased at a rate of 0.03% per year. At Ahmadabad, annual variation in average $O₃$ concentrations ranged from a least value of 12 ppb during August to the highest value of 30 ppb during November (Lal et al. [2000](#page-13-0)) (Fig. [1](#page-3-0)). Ahammed et al. ([2006](#page-12-0)) have reported highest O_3 levels during the winter and summer and lowest during the monsoon at Anantpur. Similar patterns of seasonal variation of O_3 concentration have also been observed at another rural site Gadanki (Naja and Lal [2002\)](#page-13-0). A relatively low O_3 was observed during monsoon (18.4 \pm 3.5 ppbv) than summer, winter and post-monsoon season (monitoring period November 2009 to October 2010) at Kannur, a tropical site located in coastal region of India (Nishanth et al. [2012b\)](#page-13-0). According to Beig and Brasseur [\(2006\)](#page-12-0), the relatively low amount of O_3 and its precursors during monsoon compared

City	Months/year/season	NO_v/NO_2 concentration (ppb)	Reference
Ahmadabad	1993-1996	$5.0 - 75$ (diurnal mean)	Lal et al. (2000)
Anantpur	$2001 - 2003$	3.9 ± 0.6 (annual average)	Ahammed et al. (2006)
New Delhi	January 1997–November 1998	$32 \pm 11 - 41.5 \pm 35$ (annual average)	Aneja et al. (2001)
Nagercoil	March 2007–February 2010	$3.4 - 7.7$ (monthly mean)	Elampari et al. (2013)
Tiruchirappalli (eight sites)	August 2008-January 2009	$67.4 - 90.2$ (24 h)	Horaginamani and Ravichandran (2010)
Varanasi (four sites)	Summer and winter of 1998–99 and $1999 - 2000$	Summer— $11.7-80.1$ (monthly mean) Winter-28.0-47.4	Agrawal et al. (2003)
Varanasi	June $2005 -$ October 2006	$12.1 - 16.9$ (monthly mean)	Rai and Agrawal (2008)
Varanasi	December 2004–March 2005	$38.2 - 43.1$ (monthly mean)	Rai et al. (2007)
Varanasi	December 2007–March 2008	$4.5 - 6.9$ (monthly mean)	Tripathi et al. (2011)

Table 1 Trend of $NOX/NO₂$ concentrations at different locations in India

to other seasons is due to washout effects. Table [2](#page-4-0) depicts the $O₃$ concentrations at different locations in India.

Apart from general emission sources, there are also episodic emissions from various social activities in India and one such important source is from fireworks set off during the festival days (Praseed et al. [2012a\)](#page-13-0) which leads to sudden many fold increase in the O_3 precursors or O_3 itself. Apart from causing serious health hazards to humans, these increased O_3 concentrations leads to acute exposure of plants to O_3 stress. Praseed et al. [\(2012a\)](#page-13-0) investigated the air quality of Kannur, India during "Vishu" a traditional festival during April 2010 and April 2011 and observed that the concentration of O_3 were doubled during that period while $NO₂$ increased by 2.5 times compared to the concentration on days taken as control. Yerramsetti et al. [\(2013\)](#page-15-0) focused on the influence of "Diwali" festival fireworks emissions on surface O_3 and NO_x over the tropical urban region of Hyderabad during three consecutive years (2009–2011). A twofold to threefold increase was observed in the concentrations of O_3 and NO_x , during the festival phase compared to control days. Attri et al. [\(2001](#page-12-0)) reported significant increase in night time O_3 concentrations due to firecrackers burning during the festive period. Long-term trend (2005 to 2013) indicates that the annual average concentrations of both primary

Fig. 1 Representative O_3 concentrations and monitoring duration at different monitoring stations in India. Data collected are based on the available published reports

Table 2 Trend of ozone concentration at different locations in India

and secondary air pollutants have increased, exceeding the US National Ambient Air Quality Standards (NAAQS) limit, on the respective Diwali days (Saha et al. [2014](#page-14-0)).

The IGP region is an area of about $700,000 \text{ km}^2$ which is the most extensive continuous alluvial plain falling under the category of extensively farmed zones in the world (Beig and Ali [2006](#page-12-0)). High temperature, longer sunshine hours, low relative humidity, and wind pattern of IGP favor the formation of tropospheric O_3 . Moreover, IGP is one of the most polluted regions of the world in terms of gases and aerosol loading which contributes to O_3 formation (Ramanathan and Ramana [2005](#page-14-0); Ghude et al. [2011\)](#page-13-0). The highest trend of increase (3–5.6%) per decade has been observed over the densely populated IGP region, while increasing trend of 1.2–2% per decade has been observed for southern regions of India (Lal et al. [2012](#page-13-0)). Mittal et al. ([2007\)](#page-13-0) have also reported about the prevalence of very high AOT 40 in the IGP compared to rest of the Indian regions depicting higher concentrations of $O₃$ in northern than the southern regions. A multifunction regression model was utilized by Lal et al. (2012) (2012) that estimated the O_3 trend from 1979 to 1992 over the Indian region and found a trend of $0.4 \pm 0.4\%$ annual increase over the north eastern IGP region.

Figure [2](#page-5-0) shows the O_3 monitoring carried out at Varanasi situated at the northeastern IGPs for the two major crop seasons. In India, wheat is chiefly a rabi crop (December to March) while rice is a kharif crop (July to October). The data

Fig. 2 Compilation of the O_3 monitoring data of a decade (2002–2012) carried out at Varanasi for the two major crop seasons (rabi—wheatgrowing season; kharif—rice-growing season). Mean of the individual

months are given along with the seasonal mean. Data collected are based on the available published reports

provided here represents the decadal variations in O_3 concentrations in both the crop-growing seasons from December 2002 to March 2012 (Fig. 2). For the kharif season, lowest seasonal mean (33.6 ppb) was in the year 2005 and highest concentration (51.0 ppb) was in the year 2007. For rabi season, seasonal mean varied from lowest value of 38.3 ppb in 2002–2003 to highest value of 52.5 ppb during 2009–2010. A general lower value has been observed in the kharif season which represents the monsoon in India while rabi crop growth season depicted higher values often exceeding 40 ppb. It is also evident that there were higher O_3 concentrations during the reproductive phase of the plant life in comparison to the vegetative phase in both the seasons. Different stages of reproductive development are sensitive to O_3 (Black et al. [2000\)](#page-12-0) and the higher concentrations during reproductive phase perhaps may be a cause of yield reductions in IGPs by affecting different stages of reproductive development.

AOT40 is a concentration based critical levels for crops and is calculated as the mean hourly $O₃$ concentration accumulated over a threshold concentration of 40 ppb. According to the LRTAP Convention ([1996](#page-12-0)), AOT40 of 3 ppmh accumulated over 3 months was considered to be critical above which $O₃$ can cause significant yield losses. Considering the significance of AOT40, Mills et al. ([2007](#page-13-0)) also employed the crop response data to derive the O_3 dose and yield functions of 19 agricultural and horticultural crops. In Europe, AOT 40 is an exposure-response approach based on the linear decline in crop yield (Fuhrer et al. [1997\)](#page-13-0). Other workers have also shown a close linear relationship between AOT40 and yield of crop plants (Sarkar and Agrawal [2010;](#page-14-0) Rai and Agrawal [2014](#page-14-0); Singh et al. [2014\)](#page-14-0). Rai and Agrawal [\(2014\)](#page-14-0) showed reduction in yield of two wheat varieties (PBW 343 and M 533) at

ambient O_3 and reported that linear regression between relative yield and AOT40 showed 6% yield loss at AOT40 of 3 ppmh for both the cultivars. AOT40 and yield response relationship indicated a linear decline in yield resulting from cumulative exposure of O_3 and relative yield of quality protein maize (HQPM1) and nonquality protein maize (DHM117) (Singh et al. [2014](#page-14-0)). A compilation of AOT40 values reported from different studies performed in Varanasi is provided in Table [3](#page-6-0).

The burning of agricultural residues in the field particularly the rice and wheat straw is a very common agricultural practice in Northern India. This results in the emissions of VOC, CO, NO_x (0.47 Tg year⁻¹) which act as O₃ precursors and hence more photochemical production of O_3 in rural areas (Galanter et al. [2000;](#page-13-0) Oksanen et al. [2013\)](#page-13-0). A considerable temporal and spatial variation in AOT 40 values has been observed across the Indian region, and its large parts show $O₃$ values above the AOT 40 threshold limit (3000 ppbh) for 3 months (Roy et al. [2009\)](#page-14-0). Moreover, a large portion of India shows that the directive set by UNECE (UN Economic Commission for Europe) and WHO for the critical limit of AOT 40 exceeds every month (Roy et al. [2009](#page-14-0)). Such higher concentration of O_3 leads to marked reduction in the yield of various crops in India.

Yield losses in India

Debaje ([2014](#page-12-0)) estimated the yield losses of two major crops (winter wheat and rabi rice) due to surface O_3 for the period 2002–2007. It was indicated that relative yield loss (RYL) of the mean total production per year was 5 to 11% (6–30%) for

Table 3 AOT values for ambient O3 recorded at Varanasi during different crop growing seasons

Plant	AOT40 value (ppm h)	Monitoring duration per day(h)	Reference
Rice			
June to October 2005 and 2006	2.1	12	Rai et al. (2010)
June–September	11.2	12	Sarkar et al. (2015)
Wheat			
December-March	6.2	12	Rai et al. (2011b)
December 2007-March 2008	7.9	12	Sarkar and Agrawal (2010)
December 2008-March 2009	8.7	12	Sarkar and Agrawal (2010)
December 2009-March 2010	12.1	12	Rai and Agrawal (2014)
December 2010–March 2011	11.6	8	Singh et al. $(2015a)$
December 2011–March 2012	7.8	8	Mishra et al. (2013)
Maize			
December 2011-April 2012	8.4	10	Singh et al. (2014)
Mung bean			
April-June 2011	11.5	8	Chaudhary and Agrawal (2015)
April-June 2012	11.4	8	Chaudhary and Agrawal (2015)
Soybean			
July-October 2012	9.0	12	Rai et al. (2015)
Mustard			
November 2007-March 2008	7.9	12	Singh et al. (2012)
November 2010–March 2011	7.3	8	Tripathi and Agrawal (2012)

winter wheat and $3-6\%$ (9-16%) for rabi rice using M7 (AOT40) index. Sinha et al. (2015) (2015) (2015) estimated the O₃ induced yield losses based on the AOT40 metrics for wheat, rice, cotton, and maize in Punjab. RYL ranged from 27 to 41% for wheat, 21–26% for rice, 9–11% for maize, and 47–58% for cotton. The IGP is one of the most fertile zones of Asia and is well suited for the cultivation of staple cereals and legumes and hence is called the bread basket of India (Burney and Ramanathan [2014](#page-12-0)). Major portion of the studies considering impact of O_3 on plant productivity in IGP have been carried out with rice and wheat which are largest and second largest cultivated crops in India. Few other economically important crops such as soybean, mung bean, and mustard have also been studied in detail. The majority of experimental work in natural field conditions has been carried out in Eastern parts of IGPs in rural and suburban regions of Varanasi, where climatic conditions favor the prevalence of high concentrations of ambient O_3 . These studies have been performed mostly by using open top chambers (OTCs) and also by application of ethylene diurea (EDU) an antiozonant as a monitoring tool to evaluate the yield losses.

Rice is the staple crop of India as well as Southeast Asia providing 21% of the calorific needs of world's total population (Fitzgerald et al. [2009](#page-13-0)). Rice cultivars Saurabh 950 and NDR 97 showed 10.2 to 15.9% yield reduction under NFCs (ambient O_3) as compared to filtered chambers (FCs) during the years 2005–2006 (Rai and Agrawal [2008\)](#page-14-0) (Table [4](#page-7-0)). Later, Rai et al. [\(2010\)](#page-14-0) taking up similar rice cultivars reported that number of grains showed less reduction in NDR 97 than Saurabh 950 but more reduction in test weight were recorded in former than the later. Sarkar and Agrawal ([2011](#page-14-0)) have reported 31–45% yield loss in two cultivars of rice Malviya dhan 36 and Shivani under elevated O_3 (Table [4](#page-7-0)).

Wheat is the second most important food crop of India contributing nearly one third of total grain production. India occupies the second position among all the wheat-producing countries with an annual production of 78.4 million tons (Singh et al. [2015a](#page-14-0)). Most of the investigations have been carried out with wheat under ambient or elevated levels of O_3 . In these experiments, O_3 stress led to yield losses as a consequence of impaired gas exchange, increased loss of energy in defense activities (Ambasht and Agrawal [2003;](#page-12-0) Rai et al. [2007](#page-14-0)), reduced growth, accelerated senescence, and decline in viability of pollens and harvest index (Sarkar and Agrawal [2010](#page-14-0); Mishra et al. [2013](#page-13-0)). Rajput and Agrawal [\(2005\)](#page-14-0) reported yield loss ranging from 4.0 to 5.9% in cultivar HUW 468 at six different experimental sites (Table [4](#page-7-0)). A reduction of 20.7% was found in yield of M 234 cultivar of wheat grown in OTCs ventilated with ambient air (40.6 ppb O3) as compared to filtered chambers (Rai et al. [2007](#page-14-0)). Sarkar and Agrawal [\(2010\)](#page-14-0) found reductions of 11–46% in weight of grains (m^{-2}) at ambient and elevated O₃ compared to filtered

Table 4 Yield response of various agricultural crop plants to variable O₃ concentration **Table 4** Yield response of various agricultural crop plants to variable O_3 concentration

Table 4 (continued)

(continued)

chamber taken as control (Table [4](#page-7-0)). The dose-response analysis indicated 5.4% yield reduction at the European critical level of 3 ppmh (Sarkar and Agrawal [2010\)](#page-14-0). Moreover, Mishra et al. ([2013](#page-13-0)) also recognized reduction in weight of grains plant⁻¹ of tall cultivar (K-9107) and dwarf cultivar (HUW-37) and found that dwarf cultivar with higher yield potential was more sensitive to O_3 than tall cultivar with lower yield potential (Table [4\)](#page-7-0). A study was performed on maize cultivars differing in nutritional quality of the kernels; Singh et al. [\(2014\)](#page-14-0) noticed 4 –13.8% reduction in weight of kernels plant⁻¹ for DHM117 and HQPM1 cultivars.

Other major economically important crops were also found to respond similarly under the prevailing O_3 stress at IGP. Ozone responses of Vigna radiata and Brassica campestris was reported by Agrawal et al. ([2003](#page-12-0)). The species were grown within the urban fringes of Varanasi at four sites, and the respective yield reductions are provided in Table [4.](#page-7-0) In an investigation on air pollution and yield of mung bean plants, Agrawal et al. [\(2006](#page-12-0)) reported that weight of seed plant⁻¹ was lowered by 22 –79% depending on the concentration of pollutants at different sites of Varanasi as compared to the yield measured at reference site (Table [4](#page-7-0)). Ozone exposure of 70 and 100 ppb led to reductions in yield of Glycine max cultivars, and it was emphasized that the newly developed one (PK 472) was more O 3-sensitive compared to the older variety (Bragg) (Singh et al. [2010a\)](#page-14-0) (Table [4](#page-7-0)). Responses of mustard (*B. campestris*) and linseed (*Linum usitatissimum*) to O_3 were studied by Tripathi and Agrawal [\(2012](#page-15-0) and 2013), and reductions were detected in test weight of seeds and oil contents (Table [4\)](#page-7-0). In the biomonitoring study with mung bean cultivars, reductions were found in yield, and the dose-response analysis indicated towards highest sensitivity for HUM-1 and least sensitivity for cultivar HUM-23 (Chaudhary and Agrawal [2015\)](#page-12-0) (Table [4\)](#page-7-0). Interaction between nutrients (NPK) availability and O ³ stress was investigated by Singh et al. [\(2015a](#page-14-0) and 2012) taking up wheat and mustard (Table [4\)](#page-7-0). Yield losses due to ambient O_3 were detected at recommended NPK grown in NFC condition with respect to air filtration. Studies from other regions of India have also reported reductions in yield upon O_3 exposure. Bhatia et al. [\(2011](#page-12-0)) stated that the presence of higher O_3 (59.1–69.7 ppb) led to 11 to 12% decrease in the yield of rice. Singh et al. ([2013](#page-14-0)) found a decrease of 8% in the number of siliqua plant⁻¹ while weight of grains decreased by 35.9% at elevated O_3 (EO) as compared to nonfiltered air (NF) in *B. juncea*. Yield reductions of 14.3% in no. of grains \cosh^{-1} for NF treatment while a reduction of 23.3% was observed for EO (NF + 25–35 ppb O_3) as compared to controlled filtered (CF) treatment in maize (Bhatia et al. [2013](#page-12-0)).

Variations/differences in magnitude of yield reductions in different cultivars of the crops was found due to inherent plant characters (leaf area, stomatal conductance, etc.), differential allocation of photosynthates to reproductive organs and seed

filling, foliar injury, impairment to reproductive structures, variable reductions in photosynthesis and stomatal conductance and different levels in induction of antioxidative defense system. Wheat cultivar PBW 343 with larger leaf area and high stomatal conductance was more sensitive to O_3 than M533 with comparatively smaller leaf area and low stomatal conductance (Rai and Agrawal [2014\)](#page-14-0). Reproductive structure such as viable pollens and fertile florets per plant were affected more in cultivar Sonalika than HUW510, thus displaying greater reduction in yield (Sarkar and Agrawal [2010](#page-14-0)). Similarly in mustard, cultivar Sanjukta showing greater reduction in photosynthesis and reproductive structures manifested greater reductions in yield (Tripathi and Agrawal [2012](#page-15-0)). Higher reduction in number of ovules per capsule resulted in more loss in test weight in cultivar Padmini as compared to T-397 in linseed (Tripathi and Agrawal [2013](#page-15-0)). More foliar injury, reductions in green leaf area ratio and number of male flowers led to comparatively more yield loss in maize cultivar DHM117 than HQPM1 (Singh et al. [2014](#page-14-0)). Rai and Agrawal [\(2008\)](#page-14-0) and Rai et al. ([2010](#page-14-0)) suggested that rice cultivar NDR 97 utilized more photosynthate in maintaining metabolic machinery against O_3 stress resulting in less translocation of photosynthate to reproductive parts and therefore more yield loss compared to Saurabh 950. Chaudhary and Agrawal [\(2015\)](#page-12-0) found that higher resistance in mung bean cultivars towards elevated $O₃$ correlated with higher induction of antioxidative enzymes. Similar result was obtained in soybean cultivars PK472 and Bragg by Singh et al. ([2010a](#page-14-0)).

EDU as a research tool for the assessment of yield losses against ozone

EDU ([N-(2–2-oxo-1-imidazolidinyl) ethyl]-N-phenyl urea) is a chemical protectant against $O₃$ (Carnahan et al. [1978](#page-12-0)). The application of EDU as a "control" to ambient O_3 is useful to determine ambient O_3 effects in field grown plants, particularly in remote rural areas or developing regions where there are limited electricity supply and funding (Manning et al. [2011](#page-13-0); Tiwari et al. [2005](#page-15-0); Rai et al. [2015](#page-14-0)). It has been extensively used as research tool for O_3 injury, screening of cultivars as well as assessment of yield losses caused due to $O₃$ (Singh et al. [2015b](#page-14-0)). Studies using EDU as a chemical protec- \tan t to O_3 has been used in few studies in India to reveal differences among the cultivars $(O_3$ sensitive/tolerant) as detected for wheat (Singh et al. [2009c\)](#page-14-0) and black gram (Singh et al. [2010c](#page-14-0)). EDU induced yield improvement on various agricultural crop plants grown under different O_3 doses are provided in Table [5.](#page-10-0) Recently, Rai et al. ([2015](#page-14-0)) assessed the response of soybean to O_3 applying 400 ppm EDU as the soil drench and found that EDU was effective in preventing yield loss and provided protection to the growth of soybean plants.

Effects of ozone on nutritional quality

Apart from yield, nutritional quality of the agricultural products is also a major functional trait and a concern for society. It has been previously reported that O_3 exposure changes the composition of seed nutritional parameters and hence affects the product quality. Concentrations of starch, protein, P, N, Ca, Mg, and K decreased, while reducing and total soluble sugar increased in rice grains of cultivars NDR 97 and Saurabh 950 under ambient air exposure (NFCs) compared to FCs (Rai et al. [2010](#page-14-0)). Recently, Sarkar et al. [\(2015\)](#page-14-0) found negative effects of O_3 on nutritional parameters of grains resulting in a decreased content of starch, protein and N with an increased pool of total soluble sugars and reducing sugars. Mishra et al. [\(2013\)](#page-13-0) found that protein content in wheat grains decreased significantly by 18.8 and 15.3% in EO (NFC + 10 ppb O_3) in cultivars HUW-37 and K-9107, respectively, as compared to NFCs (ambient O_3). Reductions in total soluble sugars and starch content were also observed in both the cultivars grown under EO treatment as compared to NFCs.

Starch content and protein in the seeds of mung bean varied at different experimental sites (grown in peri-urban areas of Varanasi) with a trend showing that the sites having high O_3 concentration had lower starch and seed protein content (Agrawal et al. [2006](#page-12-0)). Chaudhary and Agrawal [\(2015](#page-12-0)) studied the role of O_3 in modifying the seed quality of six mung bean cultivars. Total soluble sugar and starch reduced along with protein and N. Lower Ca, Mg, and K contents were also observed in all the cultivars under elevated O_3 atmosphere. Singh et al. [\(2010c](#page-14-0)) exposed two black gram cultivars to O_3 and observed a decline in total amino acid and protein contents in the seeds.

Exposure of O_3 also changed the quantity as well as quality of oil in crop plants. Apart from reduction in protein content, oil content and fatty acid profile displayed variation in mustard seeds after O_3 exposure in test cultivars Sanjukta and Vardan (Tripathi and Agrawal [2012](#page-15-0)). Iodine and saponification values were increased with greater induction in Sanjukta as compared to Vardan. While saturated fatty acid (SFA) content was reduced after O_3 exposure; other constituents of fatty acid profile [monounsaturated fatty acid (MUFA), polyunsaturated fatty acid (PUFA), and omega 6 fatty acid] showed an enhancement (Tripathi and Agrawal [2012](#page-15-0)). The increase in PUFA and omega-6 fatty acid is not positive because high content of PUFA lowers the oxidative stability of oil leading to its lower suitability for frying purpose and increased chances of ulcerative colitis due to increased consumption of omega-6 fatty acid (Tripathi and Agrawal [2012](#page-15-0)). Significant decline in total sugar, N, and mineral nutrient (P, Ca, Mg, and Zn) of seeds were observed in the test cultivars (Padmini and T-397) of L. usitatissimum at elevated O_3 treatment (10 ppb above the ambient O_3)

Table 5 A summary of the effects of EDU application on various agricultural crop plants grown under ozone treatment

Species/cultivar	EDU concentration	$O3$ concentration	Yield parameter	Yield increment	Reference
Oryza sativa 18 cultivars Banthra site Lucknow site	300 ppm	42 ppb $(8 h)$ 46 ppb (8 h)	Net grain weight $plant^{-1}$ across 18 cultivars	25% (†) 48% $($ 1)	Pandey et al. (2015)
Triticum aestivum 'HD 2329' 'HUW 234' 'HUW 468'	500 ppm	29.2 ppb $(6 h)$	Weight of grains $(g m^{-2})$	22% (1) 27% (1) 36.3% $(†)$	Agrawal et al. (2004)
Triticum aestivum 'M 234' 'M 533'	150 ppm 300 ppm 450 ppm 150 ppm 300 ppm 450 ppm	Often exceeding 40 ppb (8h)	Weight of seeds (g plant ⁻¹)	24.8% (1) 66.9% $($ 1) 66.8% $($ 1) 18.8% $($ 1) 19.1\% $($ \uparrow) 20.5% (1)	Tiwari et al. (2005)
Triticum aestivum 'HUW234' 'HUW468' 'HUW510' 'PBW343' 'Sonalika'	400 ppm	34.2 to 54.2 ppb (8h)	Weight of seeds $(g m^{-1})$	11.2% $(†)$ 25.8% $($ 1) 20.5% (1) 1.9% $($ 1) 10.2% (1)	Singh et al. $(2009c)$
Vigna radiata 'Malviya Jyoti'	500 ppm	32.6 to 35.1 ppb (8h)	Weight of seeds (g plant ⁻¹)	32.2% $($ $\uparrow)$	Agrawal et al. (2005)
Vigna radiata 'Malviya Janpriya'	400 ppm	52.9 to 64.5 ppb (12 h)	Weight of seeds $(g$ plant ⁻¹)	32.2% $($ 1)	Singh et al. $(2010b)$
Vigna mungo 'Barkha' 'Shekhar'	400 ppm	41.3 to 59.9 ppb $(12 h)$	Weight of seeds (g plant ⁻¹)	36.4% $($ \uparrow) 35.6% $($ 1)	Singh et al. $(2010c)$
Glycine max 'Pusa 9712' 'Pusa 9814'	400 ppm	NFCs (50.5 to 58.9) $NFCs + 20$ ppb NFCs (50.5 to 58.9) $NFCs + 20$ ppb	Weight of seeds (g plant ⁻¹)	29.8% $($ 1) 33.0% $($ 1) 28.2% $($ $\uparrow)$ 29.0% (1)	Singh and Agrawal (2011)
Glycine max 'JS 335'	400 ppm	42 ppb $(12 h)$	Weight of seeds (g plant ⁻¹)	11.0%	Rai et al. (2015)
Brassica Campestris 'Kranti' 'Peela sona'	200 ppm 400 ppm 200 ppm 400 ppm	58.4 ppb (8 h)	Weight of seeds $(g$ plant ⁻¹)	7% (1) 17% (\uparrow) 59% (1) 34% $($ 1)	Pandey et al. (2014)

compared with ambient O_3 (NFC). Among the variables of oil quality, acid value and iodine value were enhanced significantly in both the cultivars; however, the saponification value was reduced. Enhancement of iodine value is an indicative of oil unsaturation and increased saponification value shows more number of carboxylic acid groups which is not good for human consumption and may have serious health implications (Tripathi and Agrawal [2013](#page-15-0)). Singh et al. [\(2013\)](#page-14-0) reported that elevated O_3 (EO) significantly decreased the oil, mineral nutrients (Ca, Zn, Fe, Mg, S), and protein content in B. campestris compared to ambient $O₃$ (NF) which served as the control. Singh et al. [\(2010a](#page-14-0)), while investigating the effect of elevated O_3 on nutrient content in pods of G. max (cv. PK 472 and Bragg), found that K, P, and N content declined in pods in T_1 (70 \pm 5 ppb O₃) and T₂ (100 \pm 5 ppb O₃) plants of both the cultivars compared to the control.

Impact of nutrient (NPK) availability and O_3 and related alterations in seed qualitative traits were studied by Singh et al. ([2009b](#page-14-0)). Reductions in nutrient elements, protein, and oil contents in seeds of mustard were recorded under NFCs (ambient O_3) at recommended NPK (RNPK) dose as compared to FCs. The percent reductions at RNPK were 12.5% for protein, 9% for N, 14% for P, 17% for Ca, 26.8% for Mg, 31% for K, and 34.8% for Zn, respectively, in seeds of plants grown in NFCs as compared to FCs (Singh et al. [2009b](#page-14-0)). In the similar type of setup, significant reductions were observed in protein, Mg, K, Zn, N, Ca, and oil contents in seeds of both the test cultivars (Vardan and Aashirvad) grown in NFCs and FCs at RNPK, but no significant changes were observed at 1.5 times recommended NPK (1.5 RNPK) (Singh et al. [2012](#page-14-0)). Genotypic differences between the two wheat cultivars (HUW 510 and LOK-1) based on the changes in

grain quality on application of RNPK and 1.5 RNPK were studied by Singh et al. ([2015a\)](#page-14-0). Though total sugar content increased, starch accretion reduced in grains of both the cultivars in NFCs compared to FCs and the reductions were higher at RNPK than 1.5 times RNPK. P, N, and K were reduced at NFCs compared to FCs at RNPK as well as 1.5 RNPK but the magnitude of impact was less at 1.5 times RNPK.

Information lacuna, mitigation strategies, and future perspectives

India's population is growing at a faster rate and to feed a growing population, it will need to increase crop yield with sustainable intensification of agriculture. Simultaneously, the rising O_3 concentration in India is a threat to its crop productivity. Though there exists an appreciable literature on O_3 -induced yield reductions for crop plants, information available are not enough considering the phytotoxicity of O_3 . Most of the studies conducted so far in relation to O_3 stress are performed either in field conditions or by using OTCs. Free Air Concentration Enrichment (FACE) studies in India are still in its infancy. FACE provides more natural conditions for the plant growth and OTCs have their own limitations. Though the environment inside OTCs approaches that of the natural field but generally it is comparatively warmer, more humid, shaded, and has altered air movement (Kimball et al. [1997](#page-13-0)). Moreover, experiments carried out in OTCs often overestimate treatment effects on biomass production and yield (Long et al. [2005\)](#page-13-0). The plant responses that have been tested are predominantly physiological and biochemical; therefore, there is a pressing need to expand these studies at gene/protein level to unveil the molecular mechanism behind O_3 toxicity.

In India, few more monitoring stations should be set up, which can monitor O_3 for long term to generate meaningful information. A more comprehensive surface O_3 monitoring network suggested by Ghude et al. ([2014](#page-13-0)) can be employed to investigate the origins of pollution. Mitigation efforts for limiting the O_3 precursor's emissions (particularly NO_x) should effectively be implemented. Present air quality standards need to be validated and improved.

To quantify the impacts of O_3 on crop yield at national and regional scale, National Crop Loss Assessment Network (NCLAN) program in USA and European Crop Loss Assessment Network (EUCLAN) in Europe were conducted. Such programs at national level if promoted in India can generate a lot of important information regarding the crop losses occurring in India due to O_3 pollution and would be helpful in formulation of some policies to curb the emissions of O_3 precursors. Also, there is no set up of critical limit or dose-response relationships for Indian plants like those in Europe and North America (Wang and Mauzerall [2004;](#page-15-0) Emberson et al. [2009\)](#page-12-0). So, more accurate determination of O_3 exposure and dose response relationship should be carried out to set up the critical limit for Indian plants.

Responses of plants to air pollutants vary with the supply of mineral nutrients such as NPK which is an eco-friendly solution (Singh et al. [2005\)](#page-14-0). Therefore, application of suitable level of NPK should be promoted in the field. EDU is a useful research tool to estimate crop losses especially in high $O₃$ under field conditions where electricity and infrastructure are the limiting factors (Singh et al. [2015b](#page-14-0)). So, its accessibility should be promoted in rural areas as EDU can better reveal the differences among the cultivars (Oksanen et al. [2013\)](#page-13-0) and hence help in screening of tolerant/resistant cultivars to find their suitability for cultivation in the areas having high concentrations of O_3 .

It is noteworthy that to minimize the yield losses, future crop productivity may depend on utilization of O_3 -tolerant cultivars or else developing O_3 -resistant cultivars either through conventional breeding methods or by the utilization of recent biotechnological tools. Hence, there should be large scale screening of local cultivars for their O_3 sensitivity/ tolerance taking economically important crop species as well as the unexplored species. Simultaneously, some early maturing varieties can be deployed which could face shorter growth period (Ghude et al. [2014\)](#page-13-0) escaping from cumulative O_3 exposure that larger duration crops are forced to encounter. In the long-term scenario, farmers may select/more pollution resilient or tolerant cultivars to minimize the crop losses.

Conclusions

Ozone in troposphere is a serious problem of concern due to its phytotoxicity causing yield reductions in India. Emissions of NO_x , an important O_3 precursor, are increasing in India which is responsible for an escalation of O_3 concentration over Indian regions. Higher levels of $O₃$ during summer and winter seasons are experienced whereas lowest $O₃$ formation is noticed during monsoon. Such variations over India are mainly due to higher levels of precursors and the availability of ample solar radiation in winter and summer. A low O_3 during monsoon can be attributed to weather pattern as well as washing out of O_3 precursors. This seasonal variation in O_3 concentration also varies from region to region. A general tendency of high O_3 formation can be seen over IGPs as compared to other parts of India. Prevalence of high O_3 in India results in yield losses of economically important crops as well as affects their nutritional quality. So, in view of rising O_3 problem in India, some mitigation steps should be taken urgently for reducing the O_3 precursors, developing new O_3 - resistant varieties and by adopting recent agricultural management techniques to reduce the impact of O_3 on staple crops for ensuring food security.

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