# Impact of Tropospheric Ozone on Crop Plants

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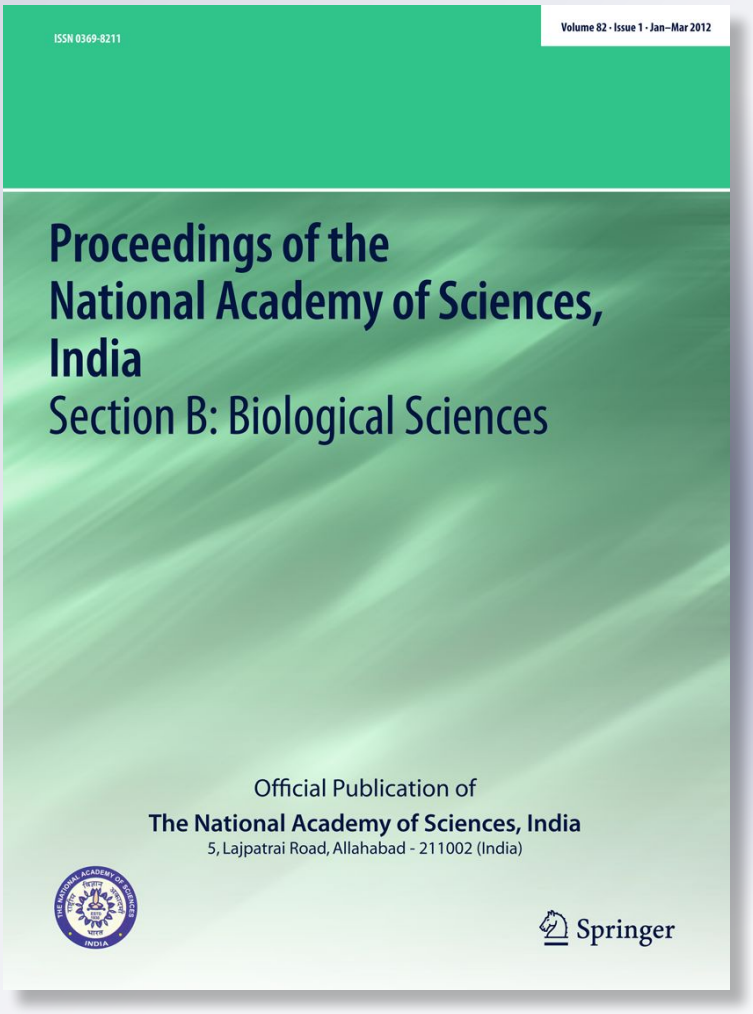


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REVIEW

# Impact of Tropospheric Ozone on Crop Plants

**Richa Rai · Madhoolika Agrawal**

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**Abstract** Tropospheric ozone ($O_3$) is the most important regional atmospheric pollutant causing risk to food production across the globe due to its phytotoxicity and prevalence over agricultural areas. Peak $O_3$ concentrations have declined in Europe and North America due to reductions in precursors during the last decades, however, emissions of $O_3$ precursors have increased in Asia. The current critical level of ozone is determined by the threshold for yield loss which is based on the seasonal sum of the external concentration above 40 ppb. In the present article, the impact of tropospheric $O_3$ on crop photosynthesis, defense mechanism, growth, reproductive processes and yield of crop plants have been documented. $O_3$ upon its entry into the leaf intercellular spaces rapidly forms reactive oxygen species and reacts with components of the leaf apoplast to initiate a complex set of responses that constitute variable countermeasures by antioxidative enzymes. Ozone affects photosynthetic process by influencing photosynthetic pigments, chlorophyll fluorescence kinetics and electron transport as well as carbon fixation in terms of decreased Rubisco activity and quantity. Translocation and allocation pattern of photosynthate also get influenced under $O_3$, which affect reproductive processes and yield of crops. Plant species and cultivars exhibit a range of sensitivity to $O_3$, which is identifiable in terms of biochemical, physiological, molecular and yield responses. Hence, understanding of cultivar sensitivity in context to $O_3$ would be helpful in development of potential $O_3$ biomarkers and $O_3$ tolerant variables.

R. Rai · M. Agrawal (✉)
Department of Botany, Banaras Hindu University, Varanasi, India
e-mail: madhoo58@yahoo.com

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## Introduction

Environmental issues have emerged as major concern for survival and welfare of mankind at the end of the twentieth century. One of the most important environmental problems of the modern world is the alarming rate of increase in air pollutant concentrations. During the past a few decades, the problem of tropospheric $O_3$ as an air pollutant has intensified several folds and assumed global concern. Tropospheric $O_3$ is recognized as the most important air pollutant affecting crop productivity losses in most parts of the world [1–5] and hence is a major threat to global food security to feed the growing population [6]. Ozone injury to crops has been widely reported in North America and Europe. The increasing emissions of reactive hydrocarbons and nitrogen oxide in urban areas have significantly increased the ground level $O_3$ concentrations. $O_3$ concentrations are found higher in rural areas than in cities, which are sources of $O_3$ [7, 8]. The first incident of photochemical smog injury to vegetation due to $O_3$ was reported by Middleton et al. [9]. Later, Richards et al. [10] found $O_3$ as a phytotoxic component of photochemical smog during investigations of leaf injury to grape vine (*Vitis vinifera*) in Southern California. Ozone after entering through stomata dissolves in the apoplast where it generates different reactive oxygen species (ROS), which are capable of altering cellular functions that cause premature senescence, cell death and up-or-down regulation of specific genes [11, 12]. The present review focuses on the aspects of $O_3$ formation, mechanism of action, growth, physiological and yield responses of crop plants.

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## Tropospheric $O_3$ Formation and its Recent Trend

Ozone is produced in planetary boundary layer (PBL), free troposphere and in the stratosphere. In the stratosphere $O_3$ is produced due to photolysis of $O_2$ by ultraviolet radiation into atomic oxygen to form $O_3$. However, in the troposphere $O_3$ formation occurs due to photolysis of $NO_2$. In the free troposphere, $O_3$ formation depends on reaction of methane, carbon monoxide (CO) and non-methane organic compounds with $NO_x$. These reactions are principally controlled by sunlight and temperature.

1. Ozone formation from $NO_x$

$$NO + 1/2O_2 \xrightarrow{HCs} 2\ NO_2$$

$$NO_2 + h\nu \rightarrow\ NO + O$$

$$O + O_2 \rightarrow O_3$$

Nitrogen dioxide diminishes when $O_3$ reaches its peak. $O_3$ concentration peaks during the late morning and early afternoon hours.

2. Ozone formation from carbon monoxide

$$CO +\ 2O_2 + h\nu \rightarrow\ CO_2 +\ O_3$$

3. Ozone formation from methane

$$CH_4 +\ 4O_2 + 2\ h\nu\ \rightarrow HCHO + H_2O + 2O_3$$

$$HCHO +\ h\nu\ \rightarrow H +\ HCO$$

$$HCO +\ h\nu\ \rightarrow H +\ CO$$

$$CO + 2O_2 +\ h\nu \rightarrow\ CO_2 + O_3$$

4. Ozone from non methane hydrocarbons

$$RH +\ 4O_2 + 2h\nu\ \rightarrow RCHO + H_2O + 2O_3$$

In the ambient air, $O_3$ precursors play important role during long range transport downwind from the sources. Polluted air masses from urban and industrial areas can affect suburban and rural areas, even reaching to remote rural areas for considerable distances. High $O_3$ levels from one particular urban area can extend as far as 48–80 km [13]. $O_3$ formation also depends upon metereological conditions. Tiwari et al. [8] reported positive correlation between mean maximum temperature/sunlight with $O_3$ concentration.

Background $O_3$ concentrations have more than doubled in the last century [14] and there is an increase in annual mean values of $O_3$ ranging from 0.1 to 1 ppb per year [15]. The US EPA has reported that emission reduction in $O_3$ precursors has been substantial over the past 29 years [16]. For the period 1980–2008, the percent decrease in emissions of nitrogen oxides ($NO_x$) and volatile organic compounds (VOC) were 40 and 47 %, respectively. Due to these emission reductions, many of the higher hourly average $O_3$ concentrations experienced during 1980 s have been reduced. Lefohn et al. [17, 18] applying three $O_3$ exposure metrics, i.e. the annual 2nd highest 1 h average concentration, annual 4th highest daily mean 8 h assessing the effects of surface $O_3$ on human health and 24 h W—126 (cumulative health index) during the period 1980–2005 and 1990–2005 found relative reduction in the peak and hourly average $O_3$ concentrations. The data of the period 1980–2008 and 1994–2008 were also explored to assess the $O_3$ patterns at 12 major metropolitan cities and 15 rural sites. In general all the $O_3$ exposure metrics showed decreasing trends or no trends. The sites of metropolitan cities showed decreasing trend of $O_3$, while rural sites showed increased $O_3$ concentration such as data from Lassen Volcanic National Park (NP), Yosemite National Park (NP) and Grand Canyon National Park (NP) showed upward shift in $O_3$ values (50–60 ppb from 30 to 40 ppb) in the month of January and February and no trends at Denali National Park (NP) site in Alaska and Mount Rainier National Park (NP) site. In Canada, the Canadian Air and Precipitation Network (CAPMoN) has recorded annual median $O_3$ concentrations at Canadian background sites ranging between 23 and 34 ppb, while annual maxima varied from 63 to 108 ppb [19].

In Europe, the standard for the protection of vegetation against $O_3$ damage is expressed as a critical level of accumulated $O_3$ concentration above a threshold of 40 ppb (AOT 40) which should not be exceeded during the growing season. A major study on $O_3$ in Europe [20] published in 2005 that pooled together the monitoring data and modeling studies along whole of the Europe. The report showed that European emissions of $O_3$ precursors had decreased over the past three decades (between 20 and 40 % for $NO_x$), with even larger reductions in Russia and that peak $O_3$ concentrations had also decreased but not in a linear fashion compared with emission reductions, although peak concentration of some sites had decreased between 1 and 1.5 % $year^{-1}$ [21]. Annual European average $O_3$ concentration have increased by about 8 % since 1996, while the maximum short term concentrations showed a decreasing trend during the period 1990–2000, which is in agreement with the 29 % decreased in the $O_3$ precursor emissions in the EU (European Union) [22]. In UK, the annual average $O_3$ concentrations are predicted to reach 30–40 ppb in rural areas leading to doubling of AOT 40 (accumulated exposure over a threshold of 40 ppb) values by 2030 [15].

Emberson et al. [1] reported that large parts of South Asia experience up to 50–90 ppb mean 7 h $O_3$ concentration (M 7). Global photochemical models project that under current legislation emission scenarios, parts of Asia will experience further significant increase in $O_3$ concentration up to 2030 [23]. Meehl et al. [14] projected an increase of

20–25 % in $O_3$ concentrations between 2015 and 2050 and 40–60 % by 2100 in Asia.

In India, despite favorable climatic conditions for $O_3$ formation, very limited data from systematic monitoring of $O_3$ levels are available (Table 1). Mittal et al. [24] using HANK model reported $O_3$ concentration varying from 25 to 100 ppb over the entire Indian region. It is very clear from the Table 1 that $O_3$ concentration is continuously increasing from 1992 to 2008 with higher peaks identified in rural areas. In a field transect study at urban sites of Varanasi $O_3$ concentrations varied from 6 to 10.2 ppb during 1989–1991 [25]. During the same period, daytime $O_3$ concentrations (9 h) were reported to vary from 9.4 to 128.3 ppb at an urban site in Delhi [26]. It was observed that 10 h ground level mean $O_3$ concentrations in Delhi varied between 34 and 126 ppb during the winter of 1993 [27]. An annual average daytime $O_3$ concentration of 27 ppb and hourly concentration varied from 2-69 ppb at Pune (India) during August 1991–July 1992 [28]. Lal et al. [29] studied the pattern of $O_3$ concentrations from 1991 to 1995 at an urban site at Ahmadabad (India), and reported that daytime mean $O_3$ concentrations exceeding 80 ppb were rarely observed. Jain et al. [30] reported that the monthly average $O_3$ concentrations in summer (April–June) ranged between 62 and 95 ppb and in autumn (October–November) between 50 and 82 ppb at an urban site in New Delhi.

At suburban sites of Varanasi, 7-hourly $O_3$ concentrations varied from 23.4 to 62.4 ppb during 2002–2006. Seasonal variations in $O_3$ concentration was observed with maximum $O_3$ concentration in summer followed by winter and minimum in rainy season [8]. During growth period of wheat (November–March) mean $O_3$ concentrations (12 h) varied between 36.4 and 48 ppb at a suburban site [31] and during growth period of rice (July–October) 23.4–44.4 ppb at a rural site [7]. $O_3$ monitoring conducted by Sarkar and Agrawal [5] at a rural site of Varanasi during 2007–2008 and 2008–2009 reported mean $O_3$ concentrations of 45.3 and 47.3 ppb, respectively. In 2007–2008 $O_3$ concentration varied from 4.0 to 125 ppb and 2.0–137 ppb in 2008–2009, respectively.

## Uptake of Ozone

The phytotoxic effects of ozone depend on the ambient exposure pattern and the amount of $O_3$ diffusing into the leaves and then converting into the liquid phase within the cells and its reactivity with cellular constituents is shown in Fig. 1. Leaves are the primary route of uptake, which is controlled by the stomatal aperture and conductance to gas diffusion [32]. Ozone can also injure cuticles, but most injury takes place after entry through stomata [33]. The absorption of $O_3$ is a consequence of chemical potential gradient between atmosphere and the site of deposition, either on the foliar surface or on the cells of the leaf interior [34]. Boundary layer resistance is a function of leaf morphology (size, shape, epidermal characteristics, trichomes, etc.), orientation and wind speed. Pubescent leaf surface absorbs more $O_3$ than glabrous one [13].

Various modeling results have shown that a major factor affecting plant response to $O_3$ is stomatal conductance ($g_s$) [35]. At higher concentrations of $O_3$, stomatal closure was reported in the majority of species [36, 37]. Various other factors such as leaf temperature, water

**Table 1** Trends of tropospheric ozone concentration in India from 1989 to 2008

| Reference | City | Ozone concentration | Months/Year | Site |
|---|---|---|---|---|
| Pandey and Agrawal [25] | Varanasi | 6.0–10.2 ppb | 1989–1990 | Urban |
| Varshney and Aggarwal [26] | Delhi | 4–128.3 ppb (9 h) | 1989–1990 | Urban |
| Singh et al. [27] | Delhi | 34–126 ppb | 1993 | Urban |
| Khemani et al. [28] | Pune | 2–69 ppb | August 1991–July 1992 | Urban |
| Lal et al. [29] | Ahmedabad | | 1991–1995 | |
| Jain et al. [30] | Ahmedabad | 62–95 ppb | 1995 | Urban |
| Tiwari et al. [8] | Varanasi | | 2002–2006 | Suburban |
| | | 45.18–62.35 | Summer | |
| | | 28.55–44.25 | Winter | |
| Rai and Agrawal [7] | Varanasi | 23.4–44 ppb | Rainy | Rural |
| Singh et al. [57] | Varanasi | 41.65–54.2 | November 2006–March 2008 | Rural |
| Sarkar and Agrawal [60] | Varanasi | 41.3–59.9 ppb | July–October 2007 | Rural |
| Sarkar and Agrawal [5] | Varanasi | 45.3 ppb | December–March 2007 | Rural |
| Sarkar and Agrawal [5] | Varanasi | 47.3 ppb | December–March 2008 | Rural |

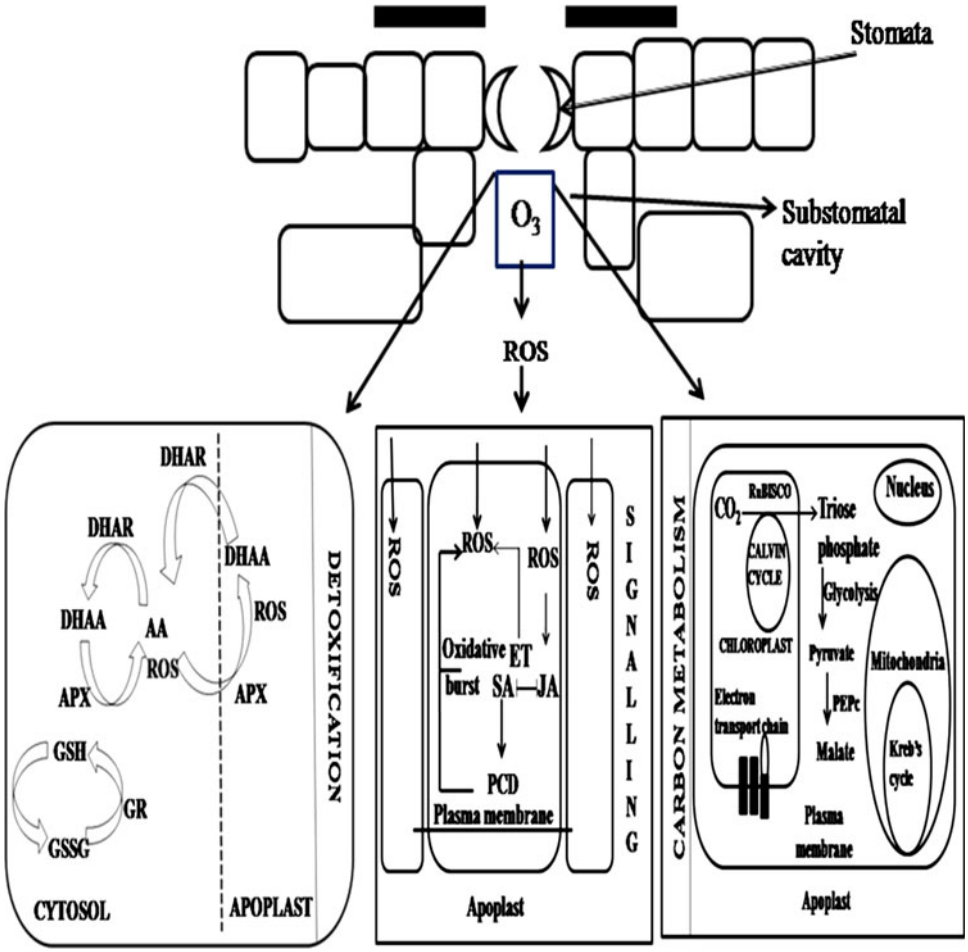


**Fig. 1** Tropospheric $O_3$: Uptake, mechanism of action, alteration of carbon metabolism, signaling and detoxification (Modified from Renaut et al. [142])

vapour pressure difference between the leaf and the surrounding air (VPD), photosynthetic photon flux density (PPFD) and soil water availability also influence stomatal conductance and thus modify the plant response to $O_3$ [1]. Stomatal conductance is higher in warm and humid environment compared to hot and dry conditions and therefore crops in warm and humid environment are more at risk to $O_3$ [38].

Heath et al. [39] proposed that with the increase in $O_3$ partial pressure in the substomatal cavity, the permeability of the guard cells is affected leading to the loss of osmotically active materials. As a consequence, internal water potential raises leading to withdrawal of water from the guard cells in favour of the subsidiary cells, causing closure of stomata. The direct effect of $O_3$ on stomatal function is correlated with its action on cell permeability [40]. Ozone increased membrane permeability to $K^+$ ions mediated through a membrane-bound $K^+$ ATPase activity [41]. Low $O_3$ concentrations affected membrane permeability of subsidiary cells resulting in water flow into the guard cells which become more turgid and led to wider opening of stomata [42].

## Formation of Reactive Oxygen Species (ROS) within the Plants

Plants have evolved systems capable of sensing and responding to environmental changes, including the elevated $O_3$ levels. The detrimental effects of $O_3$ occur due to reactions under gas and liquid phases after uptake in the plants. In gaseous phase, generation of hydrogen peroxide ($H_2O_2$) and aldehydes occur as a result of $O_3$ reactions with ethylene emissions from the plants known as ozonolysis. The products of the ozonolysis may eventually disrupt plant metabolism due to production of $H_2O_2$.

The schematic presentation of classical ozonolysis:

$$O_3 + \text{ethylene}(C_2H_4) \rightarrow \text{Aldehydes} + \text{biradical}$$

$$\text{Biradical} + H_2O \rightarrow \text{Hydroxymethyl hydroperoxide}$$

$$\text{Hydroxymethylperoxide} + H_2O \rightarrow \text{Hydroxyhydroperoxide}$$

$$\text{Hydroxyhydroperoxide} \rightarrow \text{Aldehyde} + H_2O_2$$

Mellhorn and Wellburn [43] reported that the synthesis of ethylene was intimately related to injury caused by $O_3$.

They showed that the pea seedlings at increasing concentrations of $O_3$ resulted in the higher production of ethylene and increased the foliar symptoms. Taylor et al. [44] reported that under $O_3$ stress, production of ethylene serves as a messenger for the effects on stomatal physiology and other related effects on stomatal aperture. The enhancement of $O_3$ damage in the presence of ethylene was due to direct ozonolysis of ethylene or as a consequence of the physiological changes such as modulating lesion formation and initiating premature senescence induced by ethylene [45].

Ozone after entering the leaves converts into reactive oxygen species (ROS) in liquid or aqueous phase. Ozone that has passed through leaf internal air spaces will then dissolves in the aqueous layer and react with cellular component. The breakdown of $O_3$ in pure water produces hydroxyl ($OH^{\cdot}$), peroxyl ($OH_2^{\cdot}$) and superoxide ($^{\cdot}O_2^-$) radicals, although the reactions proceed very slowly at neutral pH [46]. The degree of membrane lipid peroxidation has been correlated with higher MDA concentration [31]. $O_3$ itself can trigger the activity of a plasma membrane NADPH oxidase forming superoxide ion [47]. The mechanisms of formation of reactive oxygen species under $O_3$ interaction are given below:

$$O_3 + OH^{\cdot} \rightarrow^{-} O_2^{\cdot}(\text{superoxide radical})$$

$$O_2^- + H^+ \rightarrow HO_2(\text{peroxy radical})$$

$$HO_2 +^{\cdot} HO_2 \rightarrow H_2O_2(\text{hydrogen peroxide}) + O_2$$

$$O_2^- +^{\cdot} HO_2 + H_2O \rightarrow H_2O_2 + OH^- + O_2$$

$O_3$ reacts in the substomatal cavity with hydrocarbons such as ethylene and some terpenes [48]. This oxidative process of ozonolysis also produces $H_2O_2$ and aldehydes in a humid environment. The internal air spaces within the leaf are potential sites for $O_3$ reactions. These $O_3$ derived ROS could trigger a wide array of signal cascades, such as alterations in the physical and chemical properties of the plasma membranes to the generation of ROS. After this sensing step has occurred, signals generated at the receptors or sensors would be converted into cellular responses by means of various signal-transduction pathways. The earliest signaling events, such as protein phosphorylation or dephosphorylation and calcium influx can occur within a few minutes [49]. These changes are followed by the production of severe signaling compounds including ROS, ethylene, salicylic acid (SA) and jasmonic acid (JA) [40]. Changes in global gene expression in response to these primary and secondary signals eventually alter the metabolism and physiology of plants lead to their response to the new environment that stimulated the change. Mitogen activated protein kinase (MAPK) cascades are major pathways downstream of sensors and receptors that transducer extracellular stimuli into intercellular responses [50].

The initial site of injury caused by $O_3$ and/or $O_3$ generated ROS is the plasma membrane, resulting in changes in permeability, fluidity, potassium ($K^+$) exchange via ATPase reactions and calcium ($Ca^{2+}$) exclusion. A change in membrane function leading to a rise of intercellular $Ca^{2+}$ that would lead to alteration of all sorts of intracellular metabolism is reported [40]. The loss of $K^+$ from cells interior and rise in $Ca^{2+}$ within the cell coupled with an increased amount of $K^+$ outside the cell result in shifting of apoplastic pH, which leads to loss of a wide range of metabolites and can induce enzyme activation and alter normal gene transcription.

In contrast to $O_3$, $H_2O_2$ dissolves very well in the water phase and can be transported through the membranes and circulated within the plant. Further reactions of $H_2O_2$ lead to the formation of other reactive oxygen species such as superoxide and hydroxyl radicals, which can initiate lipid peroxidation, a chain reaction destroying the membranes [51].

## Defense Mechanism

The plasma membranes are protected by antioxidants such as hydrophilous ascorbate (Vitamin C), lipophilous α tocopherol (Vitamin E) and enzymes such as superoxide dismutase (SOD) and peroxidases (POD). The first detoxifying barrier represents the antioxidant system found in the cell (apoplasm + symplasm). The main level of defense depends on the existing content of cellular antioxidants (e.g. Ascorbate) and intensity of the detoxifying processes regenerating these metabolites. A specific pool of apoplast ascorbate is thought to react directly with $O_3$ and ROS [52]. It has been observed that within apopolasm ascorbate is easily and rapidly depleted, allowing the subsequent oxidative action of ROS in foliar cells. An efficient protective mechanism requires the transfer of ascorbate from intercellular detoxifying systems to the cell wall [52].

Ascorbic acid (AA) is an integral weapon in the defence against ROS generated by ozone (Fig. 1). In plant cells, the most important reducing substrate for $H_2O_2$ detoxification is ascorbate peroxidase, which uses two molecules of ascorbate to reduce $H_2O_2$ to water through a series of reactions known as the ascorbate–glutathione cycle [53]. An alternative mode of $H_2O_2$ destruction is via peroxidases (POD), which are found throughout the cells. Ozone tolerance due to higher ascorbate concentration has been observed in many plants such as soybean [54], snap bean ecotypes [55], rice [7] and wheat [11, 56]. An increase in POD activity has also been reported as a response to higher levels of $H_2O_2$ [7, 57].

The capacity for the regeneration of antioxidants within the cells provides second line of detoxifying barrier and is

driven by an oxidative signaling process and linked to appropriate changes in reducing power [NAD(P)H], depending on carbon metabolism changes concomitant with alteration in gene expression [58]. The summary of the relationships between stomatal uptake, metabolic changes, detoxification system and signaling under chronic $O_3$ attack in plant cells is shown in Fig. 1.

## Physiological Responses

### *Photosynthesis (Ps)*

Tropospheric $O_3$ and their generated ROS are known to alter membrane properties and membrane bound organelles like chloroplast, which lead to destruction of photosynthetic pigments [7]. Several studies have suggested chlorophyll content of leaves as an indicator of stress under $O_3$ exposure [7, 59, 60]. Destruction of photosynthetic pigments also reduces photosynthetic activity. Accelerated chlorophyll destruction is reported due to induced metabolic changes within the plant cells caused by oxidative force of $O_3$. Saitanis et al. [61] reported greater reduction in chl a compared to chl b in tobacco plants exposed to $O_3$. Greater sensitivity of chl a to $O_3$ implies a lower capacity for light harvesting as found in *Zea Mays* [62]. In a study with 20 wheat cultivars, Biswas et al. [63] found 13 % mean reductions in total chlorophyll content at 82 ppb $O_3$ for 7 h $day^{-1}$ over 21 days in OTCs.

Carotenoids are vital photoprotective agents, which prevent photooxidative chlorophyll destruction [7]. Carotenoid content is also reduced due to oxidative destruction under $O_3$ stress and leads to a decreased capacity to protect photosystem against photo-oxidation. Hence, the loss of chlorophyll and carotenoids can produce a decrease in the light absorbing capacity to develop thermal dissipation energy under $O_3$ exposures [64].

Photosynthesis, a core function in the physiology of plants is most susceptible to air pollutants. Reductions in Ps have been widely reported under ambient field conditions at higher concentrations of air pollutants [7, 36, 57, 65] (Table 2). Metadata analyses on several varieties of wheat [66], soybean [67] and rice [68] also showed varying degrees of negative response of photosynthesis under $O_3$ exposure.

Tropospheric ozone also reduces assimilation by decreasing leaf longevity and increasing senescence in

**Table 2** Changes in rate of photosynthesis (Ps) and stomatal conductance ($g_s$) of selected plants at different concentrations of $O_3$ (studies from 2000 to 2009)

| Plant | Air pollutant concentration (ppb) | Percent change increase/decrease | | Reference |
|---|---|---|---|---|
| | | Ps | $g_s$ | |
| Clover | $O_3$ 150 ppb for 3 h | (−) 37 | (−) 38 | Degl' Innocenti et al. [71] |
| Rice cv MR 84 | High $O_3$ 81.7 ppb for 8 h | (−) 53.3 | NS | Ishii et al. [77] |
| MR 185 | | (−) 45.5 | (−) 42.5 | |
| Barley cv Haider 93, Haider 91, Jou 87, Jou 85 | $O_3$ 71 ppb, $NO_2$ 30 ppb, $SO_2$ 16 ppb for 6 h | (−) 13–21 | (−) 6–12 | Wahid [79] |
| Cotton cv Giza 65 | O3 70 ppb for 10 h | (−) 18 | (−) 23 | Hassan and Tewfik [128] |
| Wheat 20 cultivars | $O_3$ 82 ppb 7 h | (−) 24 | (−) 8 | Biswas et al. [63] |
| Peanut cv NC-VII | $O_3$ 48 ppb for 12 h | (− ) 21 | NS | Booker et al. [129] |
| Soybean cv S156 | $O_3$ 60 ppb | (−) 38 | (−) 52.6 | Flowers et al. [76] |
| Wheat | CF + $O_3$ 105 ppb for 8 h | (−) 42.4 | – | Feng et al. [89] |
| Tomato cv 93.1033/1 | 150 ppb for 3.5 h | (+) 19.8 | (−) 26.5 | Degl' Innocenti et al. [72] |
| Cuor di Bue | | (−) 26.9 | (−) 43.7 | |
| Wheat 12 wild and cultivated species/ cultivars | $O_3$ 100 ppb for 7 h | (−) 36.9 | (+) 11.1 | Biswas et al. [130] |
| Rice cv Saurabh 950 | $O_3$ 35 ppb 12 h | (−) 28.3 | (−) 36.6 | Rai and Agrawal [7] |
| NDR 97 | | (−) 18.3 | (−) 52.2 | |
| Bushbean cv Camellino | $O_3$ 165 ppb for 3 h | (−) 36 | (−) 26 | Guidi et al. [73] |
| Top crop | | NS | NS | |
| Soybean cv PK 472 | O3 70 and 100 ppb for 4 h | (−) 19.8, (−) 40.4 | (−) 21, (−) 26 | Singh et al. [81] |
| Bragg | | (−) 25.6, (−) 31.6 | (−) 61, (−) 66 | |
| Wheat cv M 510 | $O_3$ 47.3 ppb 12 h | (−) 31 | (−) 9.5 | Sarkar et al. [11] |
| Sonalika | | (−) 15.5 | (−) 12 | |

(−) decrease; (+) increase; *NS* not significant

wheat plants grown in NFCs compared to FCs [60]. Loss of assimilation capacity was attributed to reduced carboxylation efficiency, which can be directly related to loss of Rubisco activity [62]. Ozone affects the synthesis as well as leads to the degradation of Rubisco due to oxidation. Non denatured Rubisco has a large number of free-sulphydryl residues. The SH groups are responsible for maintaining the correct structural conformation of Rubisco. $O_3$ induced oxidation of SH groups in Rubisco could alter the structural conformation of this enzyme, resulting in reduced catalytic activity and increased vulnerability.

$O_3$ caused reduction in level of RNA transcript for the small subunit of Rubisco (rbcS) and also decreased the expression of photosynthetic genes including Rubisco and Rubisco activase [69]. $O_3$ leads to reductions in m RNA levels of both small (rbcS) and large (rbcL) subunits of Rubisco [60]. In a proteomic analysis conducted in vivo condition on rice seedlings exposed to $O_3$ (40, 80, 120 ppb for 6 h $days^{-1}$ for 9 days), reduction in expression of Rubisco large subunit (LSU) and small subunit (SSU) was reported [70]. Agrawal et al. [69] found that $O_3$ imposes a negative effect on energy metabolism by altering gene expression of enzymes involved in energy metabolism, i.e. fructose bisphosphate aldolasechloroplast P and ATP synthase beta subunit. This leads to reduction in ATP production through photophosphorylation and thus affects the Calvin cycle in photosynthesis. Similar findings of reductions in expression of large subunit (LSU) and small subunit (SSU) of Rubisco were observed by Sarkar and Agrawal [60] in rice cultivars Shivani and Malviya Dhan 36 grown in NFCs at a rural site of Varanasi at 20 ppb above ambient $O_3$ level (51 ppb) under natural field conditions. An analysis of the documented work from 2000 to 2010 on changes in rate of photosynthesis and stomatal conductance due to $O_3$ are given in Table 2. Sarkar et al. [11] reported more reductions in Ps in sensitive cultivar of wheat than tolerant cultivar, which also showed higher reduction in $g_s$ suggesting more stomatal closure to avoid $O_3$ uptake. Rice cultivars, however, showed a contrasting response, i.e. sensitive cultivar NDR 97 showed higher Ps rate and more reductions in $g_s$ compared to Saurabh 950, a tolerant cultivar.

Biswas et al. [63] found that wild species of wheat demonstrated higher $O_3$ flux as shown by increased $g_s$ resulting in higher relative reduction in Ps rate than modern or cultivated species. Two clover cultivars *Trifolium repens* L. and *Trifolium pretense* L. exposed to 150 ppb for 3 h showed 37 % reduction in Ps and 38 % in $g_s$ in *T. repens* while *T. pretense* did not show any change in Ps and $g_s$ suggesting that tolerant cultivar performed better due to better ability of photosynthetically active mesophyll cells to cope with photo oxidative stress [71]. Similar results were recorded in two tomato genotypes 93.1033/1 and Cuor di Bue exposed to $O_3$ (150 ppb for 3.5 h) [72]. Among bush bean cultivars Camellino and Top crop exposed (160 ppb $O_3$ for 3 h), higher reductions in Ps rate was recorded in sensitive cultivar (36 %) while no change was recorded in tolerant cultivar [73]. In contrast to reduction in Rubisco activity under $O_3$ stress, Phospho enol pyruvate carboxylase (PEPcase) activity increased [58, 62]. The stimulation of PEPcase activity is related to the increase in the activities of several enzymes of glycolysis and the pentose phosphate pathway providing a higher amount of reducing power (NADPH and NADH) [62]. The reducing power is required for regeneration of antioxidants (Fig. 1).

The reduction in photosynthesis may also occur due to structural damage of thylakoids, which affects the photosynthetic transport of electron and is indicated by the reduction in Fv/Fm ratio. Fv/Fm ratio is an indicator of the photoinhibition to PS II complexes. Reduction of Fv/Fm ratio indicates an alteration of PS II photochemistry associated with a sign of photoinhibition, making plants more sensitive to light. Lowering of Fv/Fm ratio is observed in lettuce cv Valladolid (2.5 %) and Morella (2.6 %) at mean $O_3$ concentration of 60 ppb (Calatayud et al. [74]) and in white clover sensitive clone (NC-S) showed reductions of 12 % at 200 ppb $O_3$ for 5 h $days^{-1}$ in Fv/Fm ratio[75], by 9.3 % at 60 ppb $O_3$ in snap bean cv S 156 [76] and in wheat cv M 234 by 5.4 % at mean $O_3$ concentration of 42.4 ppb [31] were reported. Ishii et al. [77] also found lowering of Fv/Fm ratio in rice cv MR 84 and MR 185, at low, medium and high $O_3$ doses of 27, 55 and 87 ppb.

The reduction in Fm under ambient $O_3$ levels is ascribed to decline in the ability to reduce the primary acceptor $Q_A$ and associated increase in non-photochemical quenching. Reductions recorded in variable fluorescence (Fv) are more strongly correlated with lowering of Fm, suggesting impairment of an electron transport, which involves a recombination reaction between P 680 and reduced phaeophytin ($Phaeo^-$) within photosystem II (PS II) or directly affecting a PS II antenna system [77]. At the stage of anthesis, Meyer et al. [78] found reductions of 2–3 % in Fv/Fm at 65 ppb and 5 % at 110 ppb $O_3$ for 12 h after 14 days of exposure of flag leaves of wheat grown in closed chambers.

Under $O_3$ exposure, there are reports on wheat [31, 36, 79] and rice [7, 77] showing increase in Fo and a parallel decrease in Fm have been recorded, suggesting impairment of PS II activity [7, 11, 77]. Studies on pumpkin [80], rice [7, 77] bean [73] and tomato [72] reported increments in Fo, suggesting the inability of the reduced plastoquinone acceptor $Q_A$ to oxidize completely because of retardation of the electron flow through PS II or to the separation of light harvesting chl a/b protein complexes. This effect may be due to the inhibition of calvin cycle activity as indicated

by the reduction in $CO_2$ assimilation rates, signifying that $O_3$ increased excitation pressure on PS II reaction centres decreased the possibility of $e^-$ transport from PS II to PS I [81].

Biomass Allocation and Partitioning

Reductions in photosynthesis affect carbon assimilation, translocation and accumulation in different plant parts. The exposure of foliage to $O_3$ resulted in an accumulation of carbohydrate in the source leaves and reduced translocation to distant sink [82]. The loading of sucrose into the phloem is an active process requiring energy and high concentrations of $O_3$ have been found to reduce this process [82]. $O_3$ causes oxidation of a sensitive protein involved in phloem loading, such as sucrose translocator, hence affecting the phloem loading [83]. Under $O_3$ stress, carbohydrate pool (starch, soluble sugars and reducing sugars) is reported to be modified in wheat [79] and barley [84]. The carbohydrate pool is affected both due to reduction in the carbohydrate production and by a shift of carbohydrate to repair and replacement processes. Due to inhibition of translocation of photosynthates from source to sink, alteration in biomass partitioning occurs.

Allocation strategies for photosynthates are essential for the prediction of long term responses under pollutant stress. According to optimal partitioning models, adjustments in biomass above and below ground structures in response to environmental stresses, may serve to balance resource acquisition to maximize growth. The relative effects on the growth of different plant parts are the result of varied impacts of $O_3$ on the translocation of photoassimilates from the leaves.

Figure 2 shows the diagrammatic representation of effect of $O_3$ on photosynthate allocation. The patterns of photosynthate allocation directly affect the plant growth and reproduction. $O_3$ exposure reduced the available carbohydrates to roots in soybean [67], wheat [63], cotton [82] and a number of other crops [85, 86]. Decrease in root biomass is mainly due to injury in lower leaves, which act as the main source of photosynthates for root growth [85, 86] (Fig. 2). Allocation of carbohydrates and nutrients to new leaves is especially important in stimulating growth production [85]. Reports have also shown that chronic $O_3$ exposure also reduced carbohydrate content in leaves of rice [59], pima cotton [82] and wheat [87].

Partitioning of reducing sugars, sucrose and starch varies with different growth stages of plants. During vegetative growth stage, relatively low concentration of $O_3$ reduced root growth more than shoot growth in a wide range of plant species [85]. In normal conditions, at the time of flowering and as seeds or fruits develop, these reproductive organs generate a high demand for

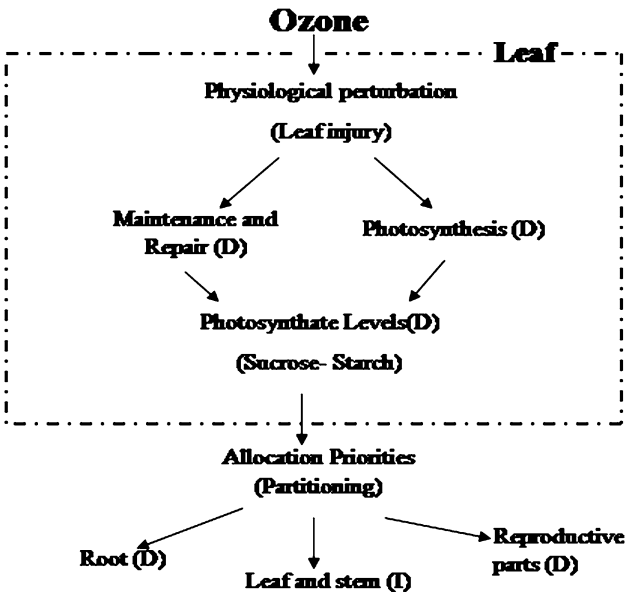


**Fig. 2** Impact of $O_3$ on metabolism, modifying the biomass partitioning. *D* decrease, *I* increase (modified from Heck et al. [143])

photosynthates, hence photosynthates are diverted from leaves and roots towards reproductive organs. Ozone reduces the number of flowers, fruits and/or seeds, but the remaining reproductive organs are often able to attain normal or larger sizes [85, 88].

In cereals, flag leaf acts as an active assimilate source during the anthesis stage of the plant. Flag, penultimate leaf sheath and peduncle photosynthesis provides assimilates for the grain, but flag leaf blade and spikes are the most important contributors to grain filling [89]. Meyer et al. [78] found an increase in carbohydrate concentrations of wheat flag leaves fumigated with $O_3$ at anthesis due to interference in transport processes (sugar transfer to conducting elements and/or phloem loading) caused by membrane damage of mesophyll or companion cells. Grandjean and Fuhrer [90] showed evidence of an ozone-induced enhanced senescence of the flag leaves, expressed as a loss of chlorophyll and soluble proteins and as an earlier peak in the activity of the enzyme glutamate dehydrogenase, which is involved in the redistribution of amino acids from leaf proteins to the grains during senescence. These changes were associated with reductions in the rate and in the duration of the biomass increase of the ears. Furthermore, Pleijel et al. [91] presented a strong correlation between an ozone-induced reduction of the flag leaf duration, expressed as chloroplast breakdown and grain yield loss in wheat. This indicates that the effects of ozone on the duration of assimilate production and grain filling was a key factor behind the yield reduction. Effect of ozone on the rate of grain filling may, however, also contribute to a reduced grain yield [92]. Gelang et al. [92]

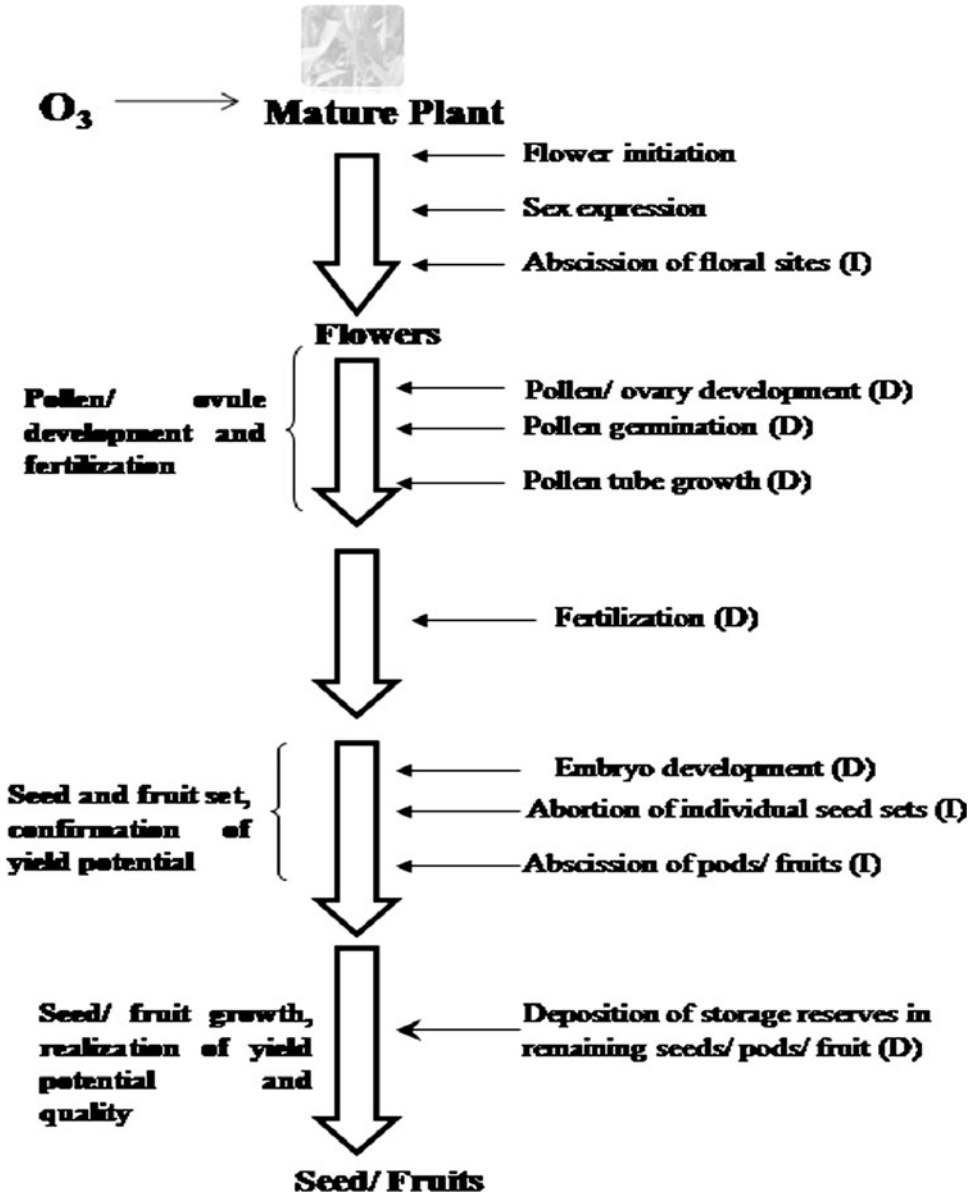


**Fig. 3** Ozone affecting the sexual reproductive processes in higher plants. *D* decrease, *I* increase (modified from: Black et al. [88])

found flag leaves senesced earlier and the grain-filling duration was significantly shorter at higher ozone exposure compared to filtered chambers (FCs) (−5, −13 and −18 % in NF1, NF2 and NF3 respectively).

## Reproductive Processes

Exposure to $O_3$ induces negative impact on reproductive processes (Fig. 3). These include modulation of pollen or ovule maturation, changes in the timing, rate or number of flowers produced, effects on seed and fruit development, yield, seeds germinability and seedling vigour[80]. Feder and Shrier [93] showed that $O_3$ altered topography of stigmatic surface. The availability of viable pollen and sufficient number of pollen grain germination and the successful growth of the pollen tube on the ovule are of crucial importance for sexual reproduction as shown in Fig. 3.

Pollen germination and/or tube growth are adversely affected by $O_3$ exposure [93, 94] (Fig. 3). Black et al. [95] found alterations in inflorescence characteristics of mustard. Flower production reduced and flower abortion increased in *Brassica campestris* [95] Number of infertile florets increased in *T. aestivum* [96] under elevated $O_3$. Impact of $O_3$ on the timing of flowering affects the seed setting as in some species flowering is closely synchronized with the presence of appropriate pollinator species (Fig. 3). Experiments have shown that $O_3$ exposure delayed flowering time in soybean [97] and cotton [98] leading to reductions in yield.

Ozone induced changes or alterations of reproductive sites may damage the embryo directly by affecting either the embryo itself, or the pollen and ovule which combine to form the embryo [95]. Even, the changes in the supply of or competition for assimilates or in the synthesis and distribution of hormones required for the successful seed development and maturation, may affect the yield under $O_3$ stress [88].

Studies have shown that $O_3$ exposure reduced yield in grain crops by decreasing ear and pod numbers [57, 95]. Grain yield in cereals is reduced by the effect of $O_3$ on rate and the duration of grain filling and due to impairment of production in carbohydrates and translocation of assimilates from the source organs to the grains [92]. Meta analysis conducted by Feng et al. [66] reported mean wheat yield reductions of 29 % at elevated $O_3$ with a range of 31–200 ppb collected from database of studies from Web of Science and AGRICOLA related to wheat photosynthesis, growth, yield and its components and grain quality responses between 1980–2007. The large yield loss was caused by a combination of decrease in individual grain weight (−18 %), ear number plant$^{-1}$ (−6 %), and grain number ear$^{-1}$ (−11 %). Results of meta analysis clearly suggest that among the growth processes, grain filling was most damaged by elevated $O_3$.

## Crop Loss Assessment Studies

Tropospheric $O_3$ was found to adversely affect the growth and yield of a variety of agricultural plants. Tropospheric $O_3$ reduced the marketable yield of a range of crop species even in the absence of visible injury, primarily through its effects in reducing photosynthetic rates and accelerating leaf senescence [38]. Impacts of tropospheric $O_3$ on agriculture is evaluated mainly on open top chamber studies, assessment of $O_3$ injury using EDU and most recent Free air concentration enrichment (FACE) studies.

### *Open Top Chamber Studies*

To quantify the impacts of $O_3$ on crop yield at national and regional scales, NCLAN (National crop loss assessment network) programme in USA and EUCLAN (European crop loss assessment network) in Europe were conducted using open top chambers. Tingey et al. [99] showed that yield reductions are highly variable, depending upon species and year. Variations observed in corn yield loss was least variable, ranging from 1 to 20% per year. In NCLAN programme, most experimental studies have used the chambered field approach as open top chamber (OTC) modified for field use with crops by Heagle et al. [100]. Data from NCLAN exposure-crop response regression analyses indicated that at least 50 % of the species/cultivars tested were predicted to exhibit 10 % yield loss at 7 h seasonal $O_3$ concentrations of <50 ppb. Adams et al. [101] estimated that yield losses due to $O_3$ exposures accounted for 2–4 % of the total US crop production. During the EUCLAN programme conducted in nine countries of Europe on a variety of crops including wheat, barley, beans, etc., the crops were grown in open top chambers and experimental results showed that yield reductions were highly correlated with cumulative exposure to $O_3$ above a threshold of 30–40 ppb during daylight hours. A cumulative indicator of $O_3$ exposure above 40 ppb threshold (AOT 40) was therefore established.

European researches on crop yield loss assessment suggested a concept of 'critical level' (CL) for evaluation of the impact of $O_3$ which is based on a cumulative exposure above a cutoff concentration below which only an acceptable level of harm is incurred. The AOT 40 associated with a 5 % yield reduction of wheat was suggested to be the most 2.96 ppm h appropriate value for CL for $O_3$. The critical level (AOT 40) required for 5 % reduction in yield for watermelon was 1.56 ppm h, for wheat 2.96 ppm h, pulses 3.03 ppm h, for cotton 3.31 ppm h, for turnip 3.47 ppm h, for tomato 3.62 ppm h, for onion 4.13 ppm h, for soybean 4.31 ppm h and for lettuce 4.63 ppm h [102]. These crops were categorized sensitive crops as critical levels were less than 5 ppm h. For moderately sensitive crops sugar beet, potato, rapeseed and tobacco critical levels ranged between 5 and 10 ppm h. Rice, maize, grape and broccoli were categorized as moderately resistant crops and critical levels ranged between 10 and 20 ppm h. The yield reductions observed for different plants were 13 % winter wheat [96], 5–31 % for bean [103] and 8.4 % for potato [104] from different countries of Europe.

The concept of AOT 40 forms the basis of the "Level 1" analysis of the potential risk of $O_3$ on plants in Europe. However, the level 1 approach does not consider influence of $O_3$ dose and vegetative response. To estimate the yield loss caused by $O_3$ accurately "Level 2" approach was established. In Level 2, those parameters that influence the flux of $O_3$ into the plant and which are critical in converting $O_3$ exposure to $O_3$ dose are given importance [105]. In Level 2 critical levels, the models were planned on response functions, based on stomatal $O_3$ uptake-yield response relationship. The model is based on the multiplicative algorithm of stomatal conductance ($g_s$) developed by Emberson et al. [106] tested on wheat, potato, grape and clover. Results showed that 5 % yield loss level was associated with 0.3 mmol m$^{-2}$ s$^{-1}$ cumulative uptake of $O_3$, approximately for wheat and 1.6 mmol m$^{-2}$ s$^{-1}$ for potato suggesting that the stomatal conductance of potato is larger than wheat. Further the, duration of exposure for $O_3$ is longer for potato than wheat, hence potato seems to be less sensitive than wheat [107].

Emberson et al. [108] reported higher magnitude of increase in global background concentrations in parts of Asia, Latin America and Africa with trends of increased emissions of ozone precursors. In Pakistan, 29–47 % yield reductions were reported for 6 varieties of wheat [109, 110], 28–42 % for five varieties of rice [111] and 37–46 % for 2 varieties of soybean [112] due to different air pollutants in the ambient air. Exposure of $O_3$ at 80 ppb concentration for 1.5 h daily for 30 days showed yield reductions of 29.5 % in *Vicia faba*, 20.6 % in *Oryza sativa*, 13 % in *Panicum miliaceum* and 9.7 % in *Cicer arietinum* [113].

Various studies conducted world wide on crop yield response to air pollutants mainly $O_3$ are presented in Table 3 where values are expressed as yield per plant relative to the respective control treatments. It was observed that reductions in crop yield varied from 2 to 60 % (Table 3). Differential responses were recorded among different crops and their cultivars. Maximum reductions were found in soybean (40–60 %) followed by wheat (20–40 %), rice (10–20 %) and minimum in barley [114]. Studies by Emberson et al. [1], Feng and Kobayashi [114] and Mills et al. [115] found same trend of sensitivity, reporting legumes to be most sensitive and barley to be most resistant under $O_3$ exposure.

In open top chamber studies, wheat and soybean cultivars were studied extensively. Exposure of 70 and 100 ppb $O_3$ for 4 h $day^{-1}$ for 70 days, led to reductions in yield by 13.9, 10, 33.5 and 25 % in soybean cv PK 472 and Bragg [116]. The yield reductions in wheat cv HP 1209 and M234 at $O_3$ concentration of 70 and 100 ppb for 4 h daily for 70 days, respectively were 8, 4.7, 17 and 15.5 % [87]. Rai et al. [31] found 20.7 % reductions in yield of wheat cv M 234 grown in chambers ventilated with ambient air (40.6 ppb) as compared to filtered chamber. Analysing the cultivar sensitivity response Sarkar et al. [11] found reductions of 7, 16.7 and 22 % in wheat cv. Sonalika and 8.4, 18.5 and 25 % in cultivar HUW 510 grown in NFCs (45.3 ppb), NFCLOs (50.4 ppb) and NFCHOs (55.6 ppb) compared to FCs. Within rice cultivars reductions in yield were 10 and 14 % in Saurabh 950 and NDR 97 at ambient $O_3$ concentration of 35.5 ppb grown in open top chambers (Table 3). In a closed chamber study conducted by Ariyaphanphitak et al. [117] showed maximum reduction in rice cultivar Pathumthani exposed at 150 ppb $O_3$ as compared to other three cultivars. Among soybean cultivars Forrest and Essex highest reduction in yield was recorded in Forrest under $O_3$ exposure [54].

Morgan et al. [118] showed that a 23 % increase in $O_3$ from an average daytime ambient level of 56 ppb to the elevated level of 69 ppb, will lead to 20 % more reduction in soybean yield. Feng and Kobayashi [114] calculated that at projected $O_3$ concentration (51–75 ppb) the yield losses would be 10 % more for soybean, wheat and rice and 20 % more for bean than at present ambient $O_3$ (41–40 ppb) thus predicting that future rise in $O_3$ is a significant threat to food production in the world (Table 3).

### *Assessment of $O_3$ Injury Using EDU*

EDU (*N*-[2-{2-oxo-1-imididazodinyl} ethyl)]-*N*-phenylurea] has been used extensively to detect plant injury caused by ambient $O_3$ under bioindicator programmes [119, 120]. EDU was also potentially used as a research tool for $O_3$ injury survey work and plant response assessment in remote areas particularly in developing regions where electricity and funding are limited [121]. EDU protects plants from premature senescence, pigment degradation and helps in maintenance of higher nutrient levels to allow successful growth and reproduction [122]. Studies using EDU as a chemical protectant to $O_3$ have shown that at seasonal mean $O_3$ concentration of 60 ppb for 6 h daily during the growth period, yield reductions of up to 40 % in mung bean and 37 % to pea were recorded in rural areas of Varanasi [123]. Singh and Agrawal [124, 125] used EDU for screening cultivar sensitivity of wheat and soybean. Among five wheat cultivars (M 234, M 468, M 510, PBW 343 and Sonalika), maximum yield increment was recorded in M 468 (25.6 %) and minimum in PBW 343 (2 %) at 43 ppb mean 8 h ambient $O_3$ concentration. Soybean cultivar, Pusa 9712 showed 29.8 and 33 % increments in yield at 52 and 72 ppb of $O_3$ at 400 ppm EDU dose. Variability in response of EDU was recorded at different exposures regimes of $O_3$, EDU as afforded maximum protection at higher $O_3$ levels [125].

### *FACE (Free Air Concentration Enrichment)*

Recently FACE (free air concentration enrichment) studies are used for studying yield responses in different cultivars of wheat, rice and soybean. Zhu et al. [126] exposed four winter wheat cultivars under elevated $O_3$ with a FACE system from 2007 to 2009 viz. Yannog 19, Yangmai 16, Yangmain 15, Yangfumai 2 in 2006–2007 (mean elevated $O_3$ 56.9 ppb for 7 h), 2007–2008 (57.6 ppb) and 2008–2009 (57.3 ppb). The grain yield reductions recorded were 18.7, 34.7 and 10.1 % in Y 19. In SoyFACE experiment, 10 soybean cultivars were exposed to ambient (46.3 and 37.9 ppb) and elevated (46.3 and 37.9) $O_3$ concentrations in 2007–2008. Yield reductions varied from 11.3 to 36.8 % in 2007 and 7.5 to 16 % in 2008 in ambient and elevated $O_3$ levels [127].

## Conclusion

Ozone has long been recognised as a phytotoxic gaseous pollutant in the troposphere. Till date, unsustainable

**Table 3** Summary of yield response (in terms of relative yield) of agricultural crops grown at varying concentration of $O_3$ from 1990 to 2010

| Reference | Study site | Crops and Cultivars | $O_3$ (ppb) | Yield response (relative yield) |
|---|---|---|---|---|
| Pleijel et al. [131] | Sweden, Goteborg | Barley | NF (29 ppb) | 98 |
| Wahid et al. [110] | Pakistan | Wheat: Pak 81, Chakwal | NF (35) | 53–65 |
| Wahid et al. [111] | Pakistan | Rice: Basmati 385, IRRI 6 | NF (35) | 62–66 |
| Fiscus et al. [132] | US—Rayleigh | Soybean: Essex | NF + O3 (70–92) | 59 |
| Maggs and Ashmore [133] | Pakistan, Lahore | Rice: IRRI 6 | NFCs (40–42 ppb) | 43 |
| Ojanpera et al. [134] | Finland | Wheat | NFCs (30 ppb) | 82 |
| Meyer et al. [135] | Germany | Wheat: Nandu | CF + O3 (65 ppb) | 89 |
| Khan and Soja [136] | Austria | Wheat | 80 for 8 h for 3 months | 61 |
| Feng et al. [137] | China | Wheat | FA + 50 ppb | 89.5 |
| Ishii et al. [138] | Malaysia | Rice: MR 84, MR 185 | NF + 32.5 ppb | 63–93.7 |
| Huang et al. [139] | China | Soybean | NF (100 ppb) | 40 |
| Ariyaphanphitak et al. [117] | Thailand | Rice: Klongluang1, Pathumani 1, Gorkor 15, Khowdokmali | NF (150 ppb) | 90.9, 87.7, 88.5, 88.9 |
| Agrawal [87] | India, Varanasi | Wheat: M 234, HP 1209 | CF + 70 ppb for 8 h for 70 days | 85, 83 |
| Pleijel et al. [140] | Sweden, Goteborg | Wheat: Dragon, Lantvete | NF + O3 (40–50 ppb) | 60, 79 |
| Wahid [79] | Pakistan, Lahore | Barley: Haider 93, Haider 91, Jou 87, Jou 85 | NF (71 ppb) | 87.1, 70.4, 64, 56.1 |
| Wahid [84] | Pakistan, Lahore | Wheat: Inquilab 91, Punjab 96, Pasban 96 | NF (72 ppb) | 19, 61, 57 |
| Rai et al. [31] | India, Varanasi | Wheat: M 234 | NF (40. 6 ppb) | 79 |
| Rai et al. [4] | India, Varanasi | Rice: NDR 97, Saurabh 950 | NF (35 ppb) | 85.5, 90 |
| Singh et al. [57] | India, Varanasi | Mustard | NF (47 ppb) | 84 |
| Shi et al. [141] | China | Rice: SY 63, LYPJ | FACE (56–59 ppb) | 82.5, 85 |
| Singh et al. [116] | India, Varanasi | Soybean: PK 472, Bragg | CF + $O_3$ (70 ppb) for 8 h for 70 days | 85, 83 |
| Sarkar and Agrawal [5] | India, Varanasi | Wheat: HUW 510, Sonalika | NF (45.3) | 91.6, 93 |
| Akhtar et al. [65] | Japan, Tokyo | Wheat: Sufi, Bijoy | CF + 60, CF + 100 for 7 h for 3 months | 88.5–55.5, 66.8–54.4 |

resource utilization has turned this secondary pollutant into a major component of global climate change and a potent threat to agricultural production. The projected rates of $O_3$ increase are critically alarming and have become a major issue of concern for agriculturalists and environmentalists. Scientific evidences clearly indicate crop plants are sensitive to $O_3$ in different ways. Plant resistance to $O_3$-involves a wide array of response ranging from the molecular and cellular level to the whole plant level. Significant effects of $O_3$-have been observed in a wide range of characteristics such as early leaf senescence, decreased photosynthetic assimilation, altered stomatal behaviour, decreased growth and productivity and reduced carbon allocation to roots. Many metabolic pathways are altered by $O_3$. Genotype differences in response to $O_3$ are related to stomatal behaviour of the leaf surface and the free radical scavenging ability of endogenous antioxidant compounds in the leaf mesophyll cells.

Patterns of global exposures to $O_3$ are likely to change dramatically over the next 50 years causing a significant threat to global food production and ecosystem function. There is a dearth of such field data on estimating the impact of rising $O_3$-concentration on agriculture in developing countries. Such understanding is crucial in predicting the long-term impacts of $O_3$ in global context, including the information of cultivar sensitivity. Several potential $O_3$ biomarkers may be exploited in the future to screen and develop $O_3$-tolerant varieties.

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