4 Secondary Criteria Air Pollutants: Environmental Health Effects

Abstract

Air quality has become a serious concern in mostly urban areas and covering different parts of the world. Over the last few years, there have been tremendous studies reported so far related to harmful health effects due to bad air quality in urban areas across the globe. Among all air pollutants, criteria air pollutants are specifically highlighted for critically analysing about the environmental impacts in relation to plants species, materials, health, biosphere, etc. These air pollutants are in focus due to their toxicity, reactivities and the severity of their impacts. Among them very less information has been reported on secondary criteria air pollutant. Hence, the present chapter focuses on the nature and behaviour of secondary criteria air pollutants with respect to their impacts on environment. It will also highlight the mechanisms involved in examining their impacts, toxicity and overall assimilation plus fate of their chemical reactivities.

Keywords

Secondary criteria air pollutants · Health · Toxicity · Air quality and Biosphere

4.1 Introduction

Deleterious air quality is a main issue in both developed and developing countries. Rapid increase in motor vehicular emissions during peak traffic hours results in major air pollution episodes at selected hotspots (Nagpure et al. 2013; Mishra et al. 2015). The extreme air pollution episodes mostly occur during winter season, characterized by low winds, low mixing heights and temperature inversions (Nagpure et al. 2016; Martins et al. 2010). Many of the populous centres have large, major contribution by man-made pollutants in the atmosphere which is resulted into bad air quality not only at regional but at worldwide level. Among all the listed environmental issues, atmospheric pollution, and their impact on environmental health, is one of the most challenging issues (Chen et al. 2012). The impacts

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of different air pollutants on human health can be of various types like increased risk of lung disorders, respiratory tract problems, heart-related diseases, increase in other respiratory problems like loss of breath, coughing and increase in rate of suffering from lung disorders, impact on central nervous systems like memory loss, impacts on behavioural patterns, cancer and early-age mortality (Chen et al. 2016; Fang et al. 2003). Few sensitive people are more prone to air pollution-related disorders, for example, those suffering with already existing heart-related and lung-related diseases (such as cardiac arrest, asthma, emphysema and severe and long-lasting bronchitis), diabetes, old aged people and children. In the case of developed countries, ambient air pollutant levels decreased due to implementation of advanced and efficient management practices (Farhat et al. 2013). Nevertheless, the problem of sudden occurrence of extreme air pollution episodes still survives. Moussiopoulos et al. (2004) noticed that ambient air pollution levels at urban hotspot in 20 European cities were crossing the given NAAQS. In the UK, out of total declared air quality management areas, 33% were declared due to the increment in specified NOx, and 21% were due to exceedances of the particular PM standard (Jeong 2013). China is also facing severe air pollution problem due to inefficient emission control (Chai et al. 2014; Cheng et al. 2012). It has also been estimated that approximately 3–5 lakh people had died prematurely every year due to bad air quality in China and has achieved fourth rank in producing ill effects to the health of Chinese people after cardiac disorders, heavy smoking and stringent dieting (Pui et al. 2014). In Delhi, India, maximum hourly ozone and nitrogen dioxide concentrations of 138.4 $\mu g/m^3$, 106.6 $\mu g/m^3$ and 92.1 $\mu g/m^3$ were found during summer, winter and autumn, respectively (Kumar et al. 2015). Moreover, Chelani (2013) has also reported that 24 h average NO_2 concentration during summer as 116 $\mu g\ m^{-3}$ at one of the traffic intersection site in Delhi.

The air quality levels are analysed as per their criteria of composition and physicochemical properties of air pollutants. The major class of pollutants are NO_2, SO_2, CO, VOCs and particulate matter ($PM_{2.5}$ and PM_{10}). But, there are some air pollutants which are categorized as per their health risks, formation/transport mechanisms and air quality perspective, called as criteria air pollutants (Gurjar et al. 2008; Hu et al. 2015; Wang et al. 2014a, b; Zhang et al. 2004). There are six criteria air pollutants, viz. NO_2, SO_2, CO, PM, O_3 and Pb, which are designated under the Clean Air Act of 1971 and are more strongly suspected to be hazardous to human health and the environment (Ji et al. 2012). The widespread research on the criteria air pollutants along with their correlation with meteorological parameters and their impacts have been reported on a large scale (Chai et al. 2014; Guan et al. 2017; He et al. 2017; Hu et al. 2014; Huang et al. 2015; Ma and Jia 2016; Song et al. 2017; Wang et al. 2014a, b; Xie et al. 2015; Yin et al. 2017; Zhang et al. 2015; 2016; Zhao et al. 2016; Zhou et al. 2017). Among all criteria air pollutants, only one of them is formed by secondary process that is called as tropospheric ozone. Hence, this chapter focuses on the overview of secondary criteria air pollutants, i.e. tropospheric ozone and their impacts on environmental health.

4.2 Secondary Criteria Air Pollutant: Tropospheric Ozone

Ozone is found both in the troposphere and in the stratosphere. Stratospheric ozone layer is naturally occurring jacket of O_3 molecules, while most of the tropospheric ozone is formed via man-made sources (Aneja et al. 2000). Stratospheric O_3 is helpful in protecting biosphere, but the tropospheric O_3 is harmful for the plants and human health (Aneja et al. 1991). Ozone is heavier than air; it comes near to the earth's surface from stratosphere by vertical winds formed during electrical storms (Kasibhatla 1993). However, the tropospheric O_3 is formed when precursors like nitrogen dioxide, volatile organic compounds or carbon monoxide reacts with sunlight, and, therefore, this particular type of reaction is also called as photochemical reaction (Finlayson-Pitts and Pitts Jr. 1997). Due to high amount of oxygen present in the atmosphere, more than 90% of the air constitutes ozone. The ozone concentrations are generally high in the afternoon and comparatively less during night (Atkinson 2000). Trees are another source of VOCs. Both precursors like nitrogen dioxides and volatile organic compounds can be driven to long distances due to transboundary movements of air masses before they form ozone in the atmosphere, where it can reside for a long duration. Ozone concentrations in the atmosphere are found highest during calm and sunny days when precursors are present in urban areas. Sometimes, ozone levels are found to be high in rural areas as compared to urban areas, whereas at high altitudes ozone concentrations can be somewhat comparatively stable during the whole day and night (Seinfeld and Pandis 1998).

Tropospheric O_3 is a worldwide concern as its main ingredient of formation is hydroxyl radical ($OH^{\cdot}$) (major atmospheric reactant) and acts as a greenhouse gas. Over a long period of time, a number of atmospheric models have come into picture to understand the ozone chemistry and also to draft emission control policies (NRC 1991). Such models are very much limited to produce current levels of ozone and their precursors (hydroxyl group compounds, oxides of nitrogen and carbon-containing compounds). A number of probabilities in emission inventories, vehicular activities and chemical processes may all responsible for model limitations. The impact of wet deposition on ozone is not direct and pretty marginal and highlights majorly the washout of nitric acid and hydrogen peroxide which are storehouses of NOx and HOx. According to Giorgi and Chameides (1985), a simple scavenging mechanism for HNO_3 and H_2O_2 is enough to explain wet deposition in ozone models. Lawrence and Crutzen (1998) have reported that cirrus precipitation could be a significant sink of nitric acid in the upper troposphere.

4.2.1 Tropospheric Ozone Formation

Ozone in troposphere is produced by a series of photochemical reaction which involves its several pioneers such as CH_4, CO, NO_x and VOCs in the presence of sunlight. In urban areas, along with industrial and other man-made activities, vehicular activities also play majorly to emanations of ozone pioneers leading to ozone formation. Tropospheric ozone is not only a problem of cities and metropolitans but also a problem in rural areas. Rural areas, where wide areas of land are used for agricultural purposes, have high concentration of ground-level ozone due to transboundary movement, in spite of the fact that these areas are located far away from the original source. Two mechanisms may be blamed for higher levels of ozone in rural atmosphere. Firstly, direct ozone transportation from city areas and secondly, the transfer of its pioneers like NO_X, VOCs, CO, CH_4 and NMHCs backed by in situ photochemical ozone formation. Transportation of ozone from stratosphere to troposphere is also a source of ground-level ozone, but its involvement in ozone built-up is comparatively less (Royal Society 2008).

Formation of ozone in the troposphere takes naturally by the oxidation of carbon monoxide catalysed by hydrogen oxide ($HO_x = OH + H + Peroxy\ radicals$) and nitrogen oxide ($NO_x = NO + NO_2$) and by the oxidation of hydrocarbons present in the atmosphere. In the highly polluted areas, there is a higher concentration of these pollutants, and hence ozone is formed in higher concentrations in the surface air which is harmful and hazardous to human health (Finlayson-Pitts and Pitts Jr. 1997).

Due to various natural and anthropogenic processes, ozone is formed in the troposphere through several sources including:

- The downward movement of the stratospheric O_3 sources to ground level through free troposphere.
- Methane produced from marshy areas and wetlands reacts with natural NO_x for the in situ production of O_3.
- The reactions of volatile organic compounds with NO_x result in the photochemical production of O_3.
- Transportation of O_3 over large distances from distant pollution sources (Krupa and Manning 1998; Mittal et al. 2007; Rai and Agrawal 2012).

All these processes are illustrated in Fig. 4.1.

Ozone is produced from carbon monoxide by the following reaction:

$$CO + 2CO_2 + h\nu \rightarrow CO_2 + O_3 \tag{4.1}$$

Ozone can also be produced from methane by the following reaction:

$$CH_4 + 4O_2 + 2h\nu \rightarrow HCHO + H_2O + 2O_3 \tag{4.2}$$

$$HCHO + h\nu \rightarrow H + HCO \tag{4.3}$$

$$HCO + h\nu \rightarrow H + CO \tag{4.4}$$

$$CO + 2O_2 + h\nu \rightarrow CO_2 + O_3 \tag{4.5}$$

Due to the combustion of fossil fuels, the oxides of nitrogen are released into the air as NO (nitric oxide) which further gets converted to NO_2 (nitrogen dioxide) on reacting with ozone already present at the surface during daytime.

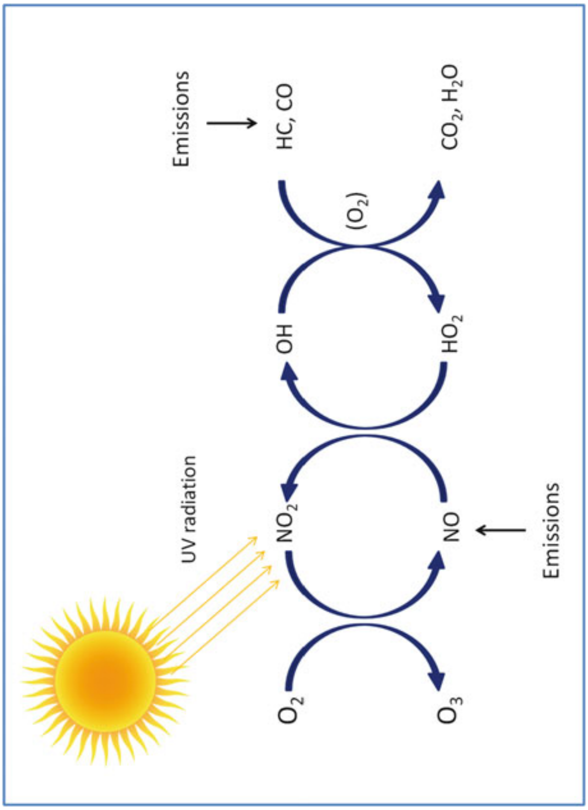

Fig. 4.1 Various mechanisms of tropospheric ozone formation

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (4.6)$$

$$NO_2 + h\nu\ (wavelength < 420\ nm) \rightarrow O(3P) \quad (4.7)$$

$$O\ (3P) + O_2\ (+M) \rightarrow O_3(+M) \quad (4.8)$$

Ozone formation also takes place using non-methane hydrocarbons

$$RH + 4O_2 + 2h\nu \rightarrow RCHO + H_2O + 2O_3 \quad (4.9)$$

4.2.2 Overall Trends of Tropospheric Ozone Levels: Present Status and Future Predicted Trends

4.2.2.1 Global Ozone Distribution

Tropospheric ozone is consistently increasing at a higher rate on global scale (Mittal et al. 2007; Rai and Agrawal 2012). In and around the nineteenth century, background ozone levels in the Northern Hemisphere became twice, approximately 35–40 ppb, and have also increased by 5 ppb approaching up to 35–40 ppb level (Royal Society 2008). In most of the countries like Latin and North America, Europe and Africa, alarmingly high levels of ozone were found and crossing the permissible limit set by WHO of 50 ppb (WHO 2006). In the case of South America and Africa, the rise of 30 ppb in ozone concentrations was documented (Zeng et al. 2008). In the area around the West Coast of the USA, ozone concentrations are reported with an increase of 0.46 ppb/year during 1985–2007 (Cooper et al. 2010). In remote farmland area of the USA, the average ozone concentration was found to be in the range of 50–60 ppb (US EPA 2006). In another study, it has been reported that a significant rise in ozone with an average trend of 0.26 ppb/year in seven different rural sites in western part of the USA was reported between the periods 1987 and 2004 (Jaffe and Ray 2007).

In spite of the fact that there is a decline in ozone emissions from man-made sources, a rise in past ozone concentrations in lower European troposphere was reported (Chevalier et al. 2007). According to the report published by the Royal Society (2008), earlier ozone concentrations in Europe are still crossing the permissible limits set by WHO and predicted to increase till 2030 partly because of hemispheric transport of ozone formation reactants from developing countries of the world. In all parts of Europe, periodic ozone event happened each year, showing a number of days of high ozone concentrations increasing beyond 50 ppb and sometimes more than 90 ppb (Hayes et al. 2007). In the case of Mediterranean region, from 2000 to 2010, out of 214 monitoring stations, only 62 stations of rural areas are showing an overall decline of 0.43%/year, whereas a steep rise of 0.64%/year was observed in city areas and 0.46%/year in suburban areas with respect to ozone concentrations (Sicard et al. 2013).

Monks (2005) summarized the monitoring and modelling studies together all over Europe and observed that emissions of ozone and their precursors had showed declined trend in Europe since the past three decades and higher significant decline was shown in Russia. In another study reported by Saitanis et al. (2015), it was reported that real-time ozone concentrations repeatedly increased by 70 ppb at Tripolis plateau in Greece. In addition to that, the highest 1 h peak ozone concentration was 240 ppb as observed in France (Pellegrini et al. 2011). An increase in average concentration of ozone was measured at an Atlantic coastal station in Ireland at the rate of 0.49 ppb/year from 1987 to 2003 (Simmonds et al. 2004) and 0.31 ppb/year from 1987 to 2007 (Derwent et al. 2007). An overall average increase of 0.14 ppb/year was reported in 13 rural sites in the UK in the period 1990–2006 (Jenkin 2008).

According to a modelling study performed by van Toumainen et al. (1996), they showed that highest hourly ozone concentration was found to be more than 50 ppb over Central Zimbabwe. Emberson et al. (2009) also showed that different parts of South Asia have reported up to 50–90 ppb average 7 h (M7) ozone concentration. Ambient air quality monitoring studies reported that average monthly ozone concentration of 50 ppb was observed generally in many parts of Asia, particularly during growth stage of various agricultural crops (EANET 2006; Xu et al. 2008). Ozone concentrations were found to be reported in various locations of the world, viz. 41.7 ppb in Xiaoji, China (Pang et al. 2009); 71 ppb in Lahore, Pakistan (Wahid 2006); and 48.1 and 47.1 ppb in Osaka and Tokyo, respectively, in Japan (Sadanaga et al. 2008). In Hong Kong too, ozone concentrations were found to be increased at the rate of 0.87 ppb/year by comparing the average during 1994–2000 and 2001–2007 (Wang et al. 2009).

Yamaji et al. (2006) has showed that highest ozone levels were found between 55 and 70 ppb during May and June in the boundary layer in the region of East China and Japan by using Community Multiscale Air Quality Model. Due to high industrialization and urbanization in the last two decades, ozone concentration was found to be higher in China as compared to other countries and the average of daywise 24 h mean ozone concentration reported to be more than 50 ppb during the crop growing season in various regions (Zhao et al. 2009; Tang et al. 2013). In 2010, in Beijing, China, during summer and monsoon months, the daily average and hourly peak ozone values at urban and rural areas were 46 and 67 ppb and 181 and 209 ppb, respectively (Wan et al. 2013). Moreover, in Yangtze Delta region of China too, a decline in mean values was observed, but a rise in daily variations in diurnal ozone values has been reported. Xu et al. (2008) observed a decrease in the average concentration but an increase in the daily variations in diurnal O_3 concentration.

4.2.2.2 Tropospheric Ozone: An Indian Scenario

The background ozone levels have increased by a rate of more than twice in the previous century with an increase of 0.1–1 ppb per year. There has been a reduction in the emission levels of NO_x and VOCs by 40% and 47%, respectively, from 1980 to 2008 due to which there has been a relative reduction in the ozone concentrations and hence an improvement in the human health (Wang et al. 2009).

There have been variations in ozone levels in India since the past few decades. Table 4.1 illustrates the ozone concentrations in different monitoring stations of

Table 4.1 Ozone concentrations at various stations in India

City	Ozone concentration (in ppb)	Period of observation
Mohali	46.5	October 2011–January 2014
Agra	30.8	September 1999–June 2001
New Delhi	28–33	Winters of 2009–2011
Allahabad	5.9–35.1	July 2002–September 2002
Varanasi	45.2	December 2002–March 2012
Mount Abu	25.5–48.8	1993–2000 (except winter season)
Ahmedabad	12–30	1991–1995
Pune	17.5–43	2003–2004
Cochin	11.8	September 1999–June 2001
Bhubaneswar	31.4	September 1999–June 2001
Berhampur	23.7	September 1999–June 2001
Anantapur	70.2	Summer 2010
Anantapur	20	Monsoon 2010
Chennai	2–53	Summer 2005
Tranquebar	8.1–25	May 1997–October 2000
Nagercoil	19.8	March 2007–February 2010

India. At Kannur, relatively low ozone levels have been observed in monsoon (18.4 ± 3.5 ppbv) as compared to that in summers, winters and pre-monsoon period (Nishanth et al. 2012). At Anantapur, highest ozone levels have been recorded during summers and winters, while the lowest have been recorded during the monsoon (Sarkar and Agrawal 2010b). Similar patterns have been observed in the rural areas also as recorded by Naja and Lal (Naja and Lal 2002) at a rural site Gadanki. In Ahmedabad, the ozone concentrations have been ranging from 12 ppb in August to 30 ppb in November (Lal et al. 2000). During 1988–1991 the surface ozone concentration at Pune was increasing at the rate of 0.03% per year as observed by Tiwari and Peshin (Ali et al. 2012). Ali et al. (2012) monitored O_3 concentrations from 1990 to 1999 at Pune and Delhi and found highest levels of ozone during summer and lowest during monsoon season. In Pune, ozone concentrations were found to be in the range of 17.5 to 43 ppb (Beig et al. 2008).

In Delhi, despite the significant short-term trends, a seasonal change is observed in the ozone concentrations in Delhi for the whole period. The mean ozone concentration for the whole period based on daily averages was 26 ppb, and the SD was 8 ppb, giving a CRV of 32%. The maximum and minimum concentrations as calculated were observed to be 64 ppb and 7 ppb, respectively, giving a range of 57 ppb. The mean ozone concentration of daily maximum values for the whole period was 62 ppb, and the SD was 32 ppb, giving a CRV of 51%. The maximum and minimum concentrations as calculated were observed to be 129 ppb and 15 ppb, respectively, giving a range of 114 ppb (Ghude et al. 2008). Ozone concentrations were found to be alarmingly higher in summer and pre-monsoon seasons as compared to winter season.

In Delhi, the ground-level ozone concentration was found to be high and crossing the permissible limits (WHO standards) in almost all the days. This is a matter of serious concern as this level of surface ozone concentrations is considered to be a health hazard. There have been clear evidences for serious ozone pollution in New Delhi. The increased levels of surface ozone can be explained on the basis of large production of photochemical ozone. Vehicular emissions of precursor gases NO_x, VOCs and hydrocarbons also serve as one of the reasons of high ozone episodes (Ghude et al. 2008).

Minimum ozone levels are observed during the monsoon period, probably because of the non-availability of sufficient solar radiations as well as washout of pollutants and consumption of ozone by HO_x radicals. High ozone levels are usually linked with meteorological factors such as sunny and warm weather, stationary wind pattern and low humidity. These favourable conditions are usually found in Delhi in the months of April to June (Mittal et al. 2007).

4.2.3 O_3 Concentrations Predictions

On the basis of modelling studies, several scientists had predicted ozone concentrations in different regions of the world. The tropospheric ozone concentrations would be expected to increase 20 to 25% by 2050 and 40 to 60% by 2100 (Meehl et al. 2007; Morgan et al. 2008). In Europe, due to the impacts of climate change, the average concentration of ozone would be around 0.9 to 3.6 ppb for the year 2029–2040 relative to the earlier concentrations that are found during 2000–2009 (Langner et al. 2012). The above-mentioned results have depicted that with drastically increased growth in O_3 concentrations, the problem of air pollution would become a global issue at the end of the middle century. Though, after the adoption of ozone precursor emission mitigation policies, high ozone concentrations are slowly decreasing in Europe, Japan and North America (Harmens 2014). Moreover, over the past 29 years, a drastic decrease in O_3 emissions has been reported (US EPA 2009). But, interestingly, most of the peak hourly mean ozone concentrations during the 1980s had been declined, but background ozone concentrations have increased. With the lack of control policies and laws, ozone precursor concentrations are still rising in developing countries as compared to developed countries (Harmens 2014; Royal Society 2008). According to the 5th Intergovernmental Panel on Climate Change (IPCC) Assessment Report, the ozone concentrations may continue to remain high by 20–25% between 2015 and 2050 and can again rise by 40–60% by the end of this century (IPCC 2014).

4.3 Impact of Tropospheric Ozone on Climate

Ozone has a very significant role to absorb IR radiation having wavelength of around 10 microns. Ozone has the property to effectively absorb IR radiation as the wavelengths present in the IR do not superimpose with water vapour and carbon

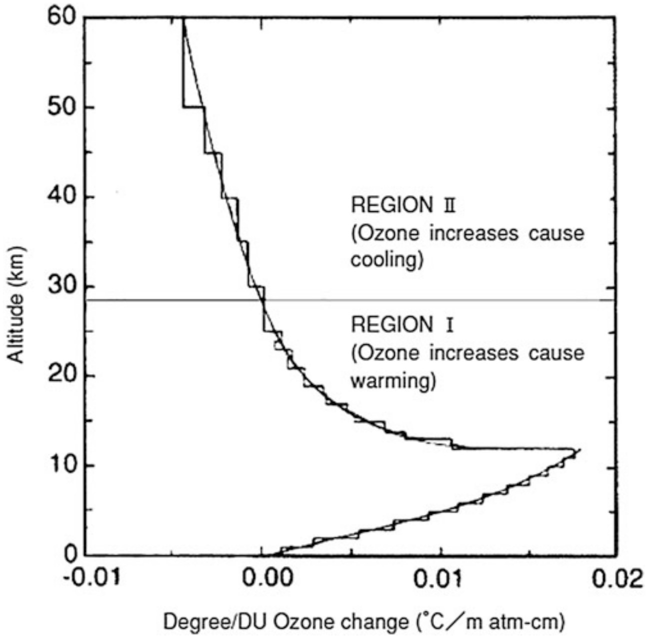

Fig. 4.2 Relationship between altitudes and variation in ambient temperature caused by rise in ozone column density (Akimoto 2006)

dioxide, and therefore, ozone plays an important role in greenhouse effect. The ozone distribution is different in different areas of atmosphere because ozone residence time in the atmosphere is short as compared with other GHGs like CO_2, and also the spatial distribution of ozone is tremendously not uniform, depending on the factors like season, altitude and area (Akimoto 2003). Figure 4.2 clearly explains the rate of change of ambient temperature with high levels of ozone concentrations at different heights. As it clearly reflects from the figure, the effect of global warming is not high at ground level. As it goes upwards towards the top of troposphere, the impact becomes more effective reaching the maximum around the tropopause that demarcates the two layers, i.e. stratosphere and troposphere, approx. 10 kms above the earth. In contrast, ozone has positive greenhouse effect in the lower layer of atmosphere. Nevertheless, at a height more than 30 kms, high ozone concentrations will lower the temperature at the ground level (Andersson and Engardt 2010).

In case of higher altitudes, where there is low temperature, the total infrared absorption by ozone is more which resulted in the increase of greenhouse effect at a greater extent. Likewise, next to the tropopause, there is lowest temperature present in the air; the greenhouse effect is at its maximum. While at greater heights in the stratosphere there is higher temperature, the total absorption of infrared radiation by ozone is decreased, resulting in greenhouse effect negative in the middle layer of the stratosphere. In brief, ozone present in the troposphere and lower layer of the stratosphere has a positive greenhouse effect. Among all the layers of troposphere, ozone has reported intense greenhouse effect in the upper troposphere (Andrey et al. 2014).

Tropospheric ozone, correlated with solar and terrestrial radiation, gives rise to change in its distribution and can form radiative forcings (RF) and lead to climate change. In the 5th Assessment Report of IPCC, it was reported that variations in ozone between 1750 and 2010 had produced a worldwide average radiative forcing of +0.40 W/m^2 (Myhre et al. 2013; Stevenson et al. 2013). The significant feature of the O_3 radiative forcing, relative to radiative forcings from uniformly mixed GHGs, is very much spatially distinct. The notable variations in ozone since 1750 have been mostly recorded in industrial regions which are major sources of ozone precursors. High industrial emissions are not only the source of ozone but also its important precursors like methane, which allows transport to decrease heterogeneities. The area-wise distribution of the O_3 radiative forcing also varies with respect to a number of factors (Song et al. 2010). The long-wave radiative forcing is the greatest where temperature changes occur between the surfaces and the tropopause attains the highest, covering the major areas of tropics and subtropics, whereas the short-wave radiative forcing is the largest over more reflective surfaces, e.g. snow or ice and desert. The existence of clouds reduces the long-wave radiative forcing and also regulates the short-wave radiative forcing. This combination of contributing factors gives rise to the net long-wave and short-wave ozone radiative forcing peaking over the southern portions of northern midlatitudes and subtropics over land and especially over Northern Africa and the Middle East (Stjernberg et al. 2012).

4.4 Impact of Tropospheric Ozone on Human Health

Inhalation and dermal exposure by ozone are the two main initial processes that are responsible for its entry in human body (Brauer et al. 2016). A number of studies have showed that routine exposure to ozone can cause DNA damage (Chang et al. 2017; Fann et al. 2012). After inhalation, ozone is accumulated in upper respiratory tract and also in intrathoracic airways (Fang et al. 2013; Fowler et al. 2009). In view of the fact that oral inhalation is responsible for less ozone removal rates than nasal inhalation, excessive physical workout leads to higher penetration into the lung. Ozone accumulation is also affected by other factors such as age and gender: greater levels of accumulation are found in children and ladies, due to the distinction in airway size (Galbally et al. 2013). Bell et al. (2014) also summarized the function of susceptibility and vulnerability factors that may affect ozone-related health effects, like gender, age, socioeconomic status and occupation. As per the opinion of scientists, age is the most significant susceptibility factor, with adults reporting major health risks with respect to ozone exposure. Scarce or constructive evidence was found for gender and occupation, with greater risks among ladies and unemployed or below poverty line people.

When ozone got accumulated or absorbed in the upper respiratory tract, it is difficult to wash out all ozone due to its less solubility in water. Instead, it dissolves in the thin layer of epithelial lining fluid (ELF). ELF constitutes a mixture of proteins, lipids and antioxidants which play as the main protector against foreign agents. Perhaps, in the reaction of ozone with ELF components, a number of products with various reactivities are formed.

According to Nazaroff (2013), exposure of children to ozone is of special significance, because such exposures might have everlasting results. It has also been found that built-up design of the body of children and adults is very much distinct in the sense that children have greater air intake per kg of mass of the body, and their airways are narrower, which makes them highly prone to air pollutants (Fischer et al. 2011). According to the US EPA (2017), chronic exposure to peak values of ozone is related to severe lung disorder. In addition to that, ozone has been related with respiratory illness, medication use, asthma and decreased respiratory functions (Cohen et al. 2017; Forouzanfar et al. 2016; Bell et al. 2014; Ainsworth et al. 2012; Anenberg et al. 2010). Simultaneously, the secondary products are also formed, when ozone reacts with ELF components, and they will cause cellular damage and disturbance in cell signalling in the respiratory system. These byproducts also cause irritations followed by exposure to ozone. There are also other important pathways which are based on the mode of action of ozone in the respiratory tract. This process is responsible for activation of neural reflexes, initiation of irritable syndromes, alteration in epithelial barrier function and sensitization of bronchial smooth muscle (Vornanen-Winqvist et al. 2018).

4.4.1 Acute Health Impacts

A number of studies are carried out on the hazardous impacts of ozone exposure. Most of the reports are well documented by WHO in recent periods (WHO 2006, 2013a, b). To represent more clearly, the degree of damage to human health and number of subjects affected are represented in Fig. 4.3. Less critical health

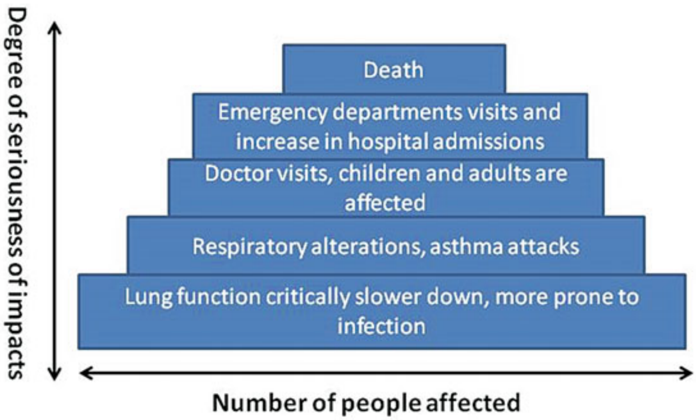

Fig. 4.3 Summary of ozone health impacts

conditions are placed at the broad base in the diagram which will affect most of the patients, while most critical ones like death or hospital admission are placed in narrow blocks which are experienced by lesser people.

The impacts of short-term exposure to ozone in relation to death rate have been found by two main latest studies: the Air Pollution and Health: A European and North American Approach (APHENA) study (Katsouyanni et al. 2009) and Public Health and Air Pollution in Asia (PAPA) study (HEI 2010, 2011). The mandate of APHENA project is to review wide range of researchers contributing and working for US and Canadian National Morbidity, Mortality, and Air Pollution Study (NMMAPS). This project also aims at analysing the data from various megacities of Canada, the USA and Europe in order to determine the variability of multiple real-time data series and to illustrate the estimate of the interrelationship of ozone increment and mortality. Likewise, the PAPA study also analyses the data of six major Asian cities (Bangkok, Hong Kong Special Administrative Region, Shanghai, Wuhan, Chennai and Delhi), and in Europe too, data was analysed of England and Wales (Pattenden et al. 2010), France (Lefranc et al. 2009), Italy (Stafoggia et al. 2010), Spain (Ballester et al. 2006) and Greece (Kassomenos et al. 2012).

Ozone also has hazardous impact on respiratory systems. The correlation between exposure and respiratory health result was explored at different conditions, like under controlled conditions during rest or in active mode, exposures in ambient atmosphere and in relation with earlier recorded pulmonary diseases like asthma or chronic bronchitis. The stimulation of short-lived reduction in lung function is among the most well-known respiratory severe end-points. Robust dataset is available for healthy young people especially passive smokers, exposed to peak levels of ozone (40–600 ppb) during workouts in ambient atmosphere (Wheida et al. 2017; Verma et al. 2017). According to WHO air quality guidelines, a new dimension of predictive models was proposed for lung function decrements (FEV1) associated with inhaled ozone exposure, with the main target to assess risk and evaluated response thresholds (Alghamdi et al. 2014; WHO 2006; Bernard et al. 1999). Major results depict that people exposed to elevated ozone concentrations which are much lesser than applied in closed chamber studies experience extreme lung function decrements (Andrade et al. 2017; ECA 2016; Bozkurt et al. 2015; Anfossi et al. 1991).

Epidemiological studies also describe about concrete, positive and important relations between variations in ambient ozone levels and increased death rate levels. The impacts of ozone were generally seen in children, elderly, asthmatics and patients with chronic obstructive pulmonary disease (COPD) (Gao et al. 2017; Glas et al. 2015). These or similar types of studies are still important as they are related to model time-related variables, such as weekend variability, seasonal impacts, air quality and weather-related parameters.

Ozone exposure also have cardiovascular disorders like enhanced heartbeat and diastolic pressure, vascular oxidative stress, irritable syndrome and decreased heartbeat variability (Fisk 2015; Bako-Biro et al. 2004; Chao 2001). On the other hand, laboratory studies on artificial exposure by ozone on human are less decisive and have provided non-uniform relations with ozone (Gilliland et al. 2001; Lee et al.

2004; Parrish et al. 2009; Manikandan et al. 2010; Kleinsorge et al. 2011; Jovanović et al. 2014; Kalimeri et al. 2016). One of the studies done by scientists in the USA in 2005 observed a 11.5% decrease in low-frequency heart rate variability (HRV) related to 2.6 μg/m^3 ozone rise in the earlier 4 h and dominant impacts noted in men diagnosed with ischemic heart disease and hypertension (Park et al. 2005). Many of the experimental studies have observed that there are positive correlations between exposure to ground-level ozone and some cardiovascular disturbances like oxidative stress, inflammation, disturbance in heart rate variability, arterial pressure, control, coagulation and myocardial infarction (Lelieveld et al. 2014; Melkonyan and Wagner 2013). In Western Europe, Nuvolone et al. (2013) observed that a 6.3% increase in outside-hospital coronary deaths for a 10 μg/m^3 rise in ozone indicates higher risks for females, adults and subjects earlier hospitalized for cerebrovascular and artery diseases.

4.4.2 Chronic Health Impacts

As compared to acute health impact studies, evidence for chronic impacts due to ozone exposure is less available. Lack of studies has been reported so far in case of long-term exposure assessment due to limitations in methodology with respect to epidemiological point of view. The most concrete relation studied so far is on effects of asthma and similar asthma symptoms. But still, more research is needed for better interpretation of findings made between ozone and long-term health end-points.

Mortality or decline in life expectancy, impacts on lung health and atherosclerosis and the early start of asthma are the most general health outcomes while analysing the health effects of chronic exposure to ozone. In 2005, WHO announced globally the recent upgradation in air quality guidelines; researchers provided sufficient proof only for short-term impact of ozone on mortality (WHO 2006). Various studies were conducted in the USA like California, and no statistically significant correlation between long-term ozone exposure and death rate was documented (Saavedra et al. 2012; Levy et al. 2005). But in the later years such as from 2012 onwards, various group studies are conducted which provided a good correlation between long-term exposure and death rate, mainly respiratory and cardiorespiratory mortality (Mullins 2018; Stowell et al. 2017; Lyng et al. 2015; Waring and Wells 2015; Schripp et al. 2012). An important initiative by the American Cancer Society Cancer Prevention Study II (CPS II) described the statistically significant correlation between long-term exposure to ozone and total death rate. Risk estimates were high for cardiopulmonary mortality (Grøntoft and Raychaudhuri 2004). Detailed analysis confirmed that long-term exposure to ozone remains connected particularly only to respiratory mortality (Carvalho et al. 2015).

Among dose exposure studies, one of the most systematic studies was the Children's Exposure Study, which occurred in 12 groups of communities present in Southern California (Bozkurt et al. 2015). A number of researchers have reported that statistically significant correlations were found between lung function and ozone annual means only among children, who are more exposed to ambient environment. A study conducted by the University of California at Berkeley has reported favourable results. UCB scientists reported long-term exposure assessment of people who live in California and found that there are stable and significant correlations between reduced airway function and long-term ozone exposure (Kalimeri et al. 2016; Darling et al. 2012). Another study which was conducted in Europe depicted the data on lung function tests two times a year on school children in various towns in Austria and Germany. Authors have found a significant correlation between ozone exposure and seasonal changes in lung function growth (Ihorst et al. 2004).

4.4.3 Guidelines for Human Health: Ozone Exposure

The 2008 Ambient Air Quality Directive implemented the highest daily 8 h average threshold of 120 μg/m^3 for health safety purpose. The possible output value at each sampling site cannot cross more than 25 days per year, calculated on 3-year average period starting from January 1, 2010 (EEA 2016). The directive also aims at long-vision approach; at each site, no value above permissible limit of 120 μg/m^3 is taken into consideration. As per the well-established evidence health impacts associated with ozone exposure, the recently updated WHO air quality guidelines set a higher strict threshold for ozone, which is a daily maximum 8 h average concentration of 100 μg/m^3 (WHO 2006).

4.5 Impact of Tropospheric Ozone on Plant Health

Ozone as a phytotoxic agent is very hazardous to the survival of plants in the observed atmosphere. Foliar injury and suppressed plant growth were the first observed negative impacts on ozone which were discovered in grape. Ozone causes damage to the stomata which is responsible for production of food through photosynthesis (Mills et al. 2007). Ozone causes alteration in the membrane properties and also is responsible for inhibition of guard cell K^+ channels (Feng and Kobayashi 2009). This results in phytotoxicity in the internal leaf tissue. Highly reactive oxygen species (ROS) which includes peroxides and free radicals may be responsible for inducing phytotoxicity (Ashmore 2005). This is because during the disease development in plants and under normal metabolic steady-state situations, oxygen gets activated and these “chain states” over time result in cell death (Volz and Kley 1988). The resulting ROS formed through ozone directly or by encouraging plant-based oxidative bursts is assumed to get toxified within extracellular spaces, but they can start reactions causing damage (Royal Society 2008; Cooper et al. 2004).

The wild plants respond to ozone with lethargic stomatal movements along with carbon dioxide concentration, vapour pressure deficit and response to light intensity variance is of lesser amplitude (Fowler et al. 1998; Pleijel 2011). Carbon allocated to different organs may get altered due to decreased assimilate supply because of photosynthesis which leads to various growth responses of the plant organs. In the priority, order shoot is given a higher priority compared to the roots and other organs used for storage like seeds, for example. As a result of this, observations showed decreased root length along with shoot weight ratios or a decrease in the ratio between total biomass produced and the yield given by the seed. Observation made in the case of crop is reduction in grain or seed yield. Ozone (O_3) injury can be indicated very well by features connected to the stomata. Ozone can be responded to by these functions either through a direct effect of ozone or a defensive mechanism of plants to ozone. For controlling the uptake of ozone by plants, stomatal conductance is treated as a vital feature (Biswas et al. 2008). Gaseous ozone entering through stomata causes cellular damage affecting mesophyll cells and also dissolves in water surrounding the cells. After entering the leaf, ozone reacts with components of apoplast and symplast. Reaction with water happens in the apoplast along with ozone reacting with ascorbic acid (AA), phenolics, transition metals and thiols giving rise to the ROS. In addition to this, introduction of ozone is also accountable for the hazards caused by ion regulation, promotes stress ethylene formation, stimulates antioxidant and phenylpropanoid metabolism and ultimately suppresses carboxylation activity and carbon assimilation. There is also a decoupling between stomatal conductance and photosynthesis resulting mainly because of ozone exposure for the long term (Broberg et al. 2015).

Ozone mainly enters inside the leaf tissues via stomata, where reactive oxygen species (ROS) is formed in huge quantity in the present aqueous medium which ultimately causes membrane permeability loss, disruption in gene expression, damage to photosynthetic proteins, loss of chlorophyll content and disturbance in plant metabolism machinery (Booker et al. 2009; Fuhrer 2009; Singh et al. 2014a, b). Increased ROS activity is observed due to exposure to high levels of ozone which produces oxidative stress that may trigger a series of complex antioxidant defence processes that can be enzymatic or non-enzymatic (Blokhina et al. 2003). Ozone is also responsible for causing decrease in photosynthetic rate (Rai and Agrawal 2012; Ainsworth et al. 2012). Therefore, decreased photosynthetic rate, enhanced defence system and secondary metabolite activities give rise to low carbon assimilation and produce significant change in carbon partitioning and decreased biomass accumulation and yield (Singh et al. 2015).

The harmful effects of ozone on growth and production of agricultural crops have been reported worldwide at a large scale and cause decline in food production rate (Ashmore 2005; Fuhrer 2009; Emberson et al. 2009; Feng et al. 2008; Feng et al. 2009; Sarkar and Agrawal 2010a, b; Singh et al. 2014a; Rai et al. 2015). After examining various results, Booker et al. (2009) found that the yield losses because of ozone lie in the range of 5–15%. At global level, yield loss of four main crops (wheat, rice, soybean and maize) because of exposure by ozone in year 2000 study was estimated to be around $14–26 billion in the USA, and $6.7 billion of crop yield loss was estimated in the case of arable crops in different parts of Europe (Van Dingenen et al. 2009). Elevated ozone concentrations are also one of the important factors in affecting the forests' health (Royal Society 2008), its productivity and economic costs (Percy et al. 2007). For the same year, in the European Union, an estimated crop yield of $ 6.7 billion was calculated for the arable crops. The increasing O_3 concentrations have also been implicated as one of the factors contributing in forest decline (Royal Society 2008). Simultaneously, ozone is also affecting semi-artificial ecosystems consisting of grasslands, declining the primary productivity of wild plants as well as floral biodiversity (Agathokleous et al. 2015; Ainsworth et al. 2012).

Another approach on impacts of ozone consists of alterations in herbivory pattern and transformations in plant interrelationships with diseases and other pathogens (Ashmore 2005). Disease transmission due to foliar pathogen on trembling aspen enhanced under high ozone concentrations in the Aspen Free Air CO_2 Enrichment (FACE) experiment resulted in the variations in leaf surface properties (Karnosky et al. 2002). In the case of similar experiment, high ozone concentrations are also responsible for affecting the performance of forest pests that are associated with variations in plant biochemistry or caused higher risk of increasing natural enemies. Long-term exposure to ozone enhances the carbon fluxes from the primary to secondary metabolic mechanisms, resulting in the formation of secondary products (Iriti and Faoro 2009), which can be responsible for causing variation in forage nutritive value, plant pathology/phytopathology, natural pest interrelationship and sometimes promoting production of invasive species (Booker et al. 2009). Ozone also plays an important role in producing disturbance in competitive ability of various plant species that after a long period of time results in alterations in the species and hereditary composition as well as functioning of semi-artificial floral ecosystems having impacts on biogeochemical cycles and carbon sequestration (Fuhrer et al. 2003; US EPA 2006; Harmens 2014; IPCC 2014). A large number of research reports on natural and non-natural communities have stated that ozone can affect the series of changes taken place in competition process and species composition (Bender et al. 2006) and the quality of more sensitive species that tends to decrease further by ozone in the whole populations because of competition relative to monoculture (Fuhrer et al. 2003). Elevated ozone concentrations are also a big reason for declining forest growth and species composition (Ashmore 2005; Wittig et al. 2009; Paoletti et al. 2010). Nevertheless, the susceptibility to natural ecosystems like forests and grasslands to high levels of ozone is already established; research on these cases are very less.

4.5.1 Ozone Relationship with Oxidative Stress and Other Physiological Responses

4.5.1.1 Ozone Generated ROS Formation and Signal Transduction

The major pathway for ozone entry into leaves is by stoma that is majorly dominated by stomatal conductance (Ainsworth et al. 2012). After ozone made its passage into the substomatal chamber, it does not reside in the apoplast for more time and instantly breaks down or reacts with the compounds existing in cell wall or apoplastic fluid to produce ROS like superoxide radicals ($O_2^{\cdot -}$), hydrogen peroxide (H_2O_2) and hydroxyl radicals ($OH^{\cdot -}$) (Laisk et al. 1989). Staining by $CeCl_3$ depicts that extracellular hydrogen peroxide accumulation was one of the oldest detectable responses to O_3 in poplar leaves exposed to 150 ppb O_3 after 1 h exposure (Diara et al. 2005).

Among the ROS, hydroxyl radical is the most reactive of oxygen species producing hazardous damages (Iqbal et al. 1996). These ROS act as early messenger molecules in signalling mechanisms, therefore choosing the downstream signalling and also triggering defence reactions in apoplast (Vainonen and Kangasjärvi 2014). These signalling molecules consists of ethylene (ET), salicylic acid (SA), jasmonic acid (JA), nitric oxide as well as mitogen-activated protein kinases (MAP kinases) (Matyssek et al. 2008). Ozone is also responsible for generation of Ca^{2+} influx within very short period of time, required for the activation of MAP kinase and NADPH oxidase. The MAPK mechanism is one of the main routes through which extracellular stimuli such as O_3 stress are embedded into intracellular cell responses. The energetic MAPK mechanism is involved in upregulation of ET synthesis. In addition to ET, biological synthesis of salicylic acid is also produced which together with ET is essential for the development of foliar injury due to exposure to high levels of ozone (Vainonen and Kangasjärvi 2014). ET and NADPH oxidase originate the transmission of oxidative energy from the region of lesion initiation to the nearby cells and resulted in cell death. After the cell death, products of lipid peroxidation act as substrate for production of jasmonic acid, which serves destructively and reduces ET-dependent lesion generation and is therefore responsible for cell death (Vainonen and Kangasjärvi 2014). An exclusive rise in ET evolution was noted in in the poplar clone "Eridana", which showed sensitivity towards O_3 (Diara et al. 2005; Vainonen and Kangasjärvi 2014). The stimulatory roles of SA and ET and the prevention of lesion expansion by JA have been explicitly characterized by the deployment of mutants of *Arabidopsis thaliana* (Vainonen and Kangasjärvi 2014). ROS is also responsible to regulate abscisic acid (ABA) that produces stomatal closure response. In the guard cells of *Arabidopsis*, ROS generated ABA synthesis and produces stomatal closure via activation of plasma membrane calcium channels (Apel and Hirt 2004). Ethylene-dependent reductions in stomatal sensitivity to ABA have also been reported by Wilkinson and Davies (2010).

4.5.1.2 ROS Defence Mechanisms: Role of Antioxidants

The abiotic stress created by ozone gives rise to oxidative damage resulted from increased production of ROS that is responsible for causing harmful impacts on cell metabolism and ultimately leads to the damage to lipids, proteins, carbohydrates and nucleic acids (Blokhina et al. 2003). To avoid stress produced by ROS, a series of antioxidant molecules are generated by (Ashmore 2005; Caregnato et al. 2013) non-enzymatic antioxidants like ascorbic acid (AA), flavonoids, phenolics, vitamin E (tocopherol), peptides (glutathiones), carotenoids, polyamines and organic buffering systems or through enzymatic antioxidants (Blokhina et al. 2003), viz. superoxide dismutase (SOD), ascorbate peroxidase (APX), glutathione reductase (GR), catalase (CAT) and different kinds of peroxidases (POD) (Caregnato et al. 2013).

Among non-enzymatic antioxidants, ascorbic acid (AA) protects complex macromolecules from oxidative bursts by directly reacting with $O_2^{\bullet -}$, H_2O_2, to give rise to α-tocopherol from tocopheroxyl and eliminate H_2O_2 by AA-GSH cycle (Pinto et al. 2003). Enhanced ascorbic acid concentrations in different crops and tree species after O_3 exposure have been reported (Lu et al. 2009; Singh et al. 2010; Yan et al. 2010; Rai and Agrawal 2014). Rai et al. (2007) documented that ascorbic acid content in wheat leaves has been increasing at the rate of 11.2% under outdoor ozone pollution. Elevated mean concentrations of ascorbic acid have been increased by 40% in 20 wheat cultivars grown in controlled chambers having exposed with 82 ppb O_3 for 7 h/day (Biswas et al. 2008). After exposed by high ozone concentrations, the variations in total ascorbic acid concentrations were found in *Psidium guajava* on the basis of leaf as an indicator and were found by Pina and Moraes (2010).

Increased ascorbic acid content was noticed in tolerant soybean cultivar PK 472 relative to sensitive cultivar Bragg at 70 and 100 ppb O_3 for 4 h from germination to growth stage (Singh et al. 2010). Ozone-sensitive (NC-S) and ozone-resistant (NC-R) plants of *Trifolium repens* and *Centaurea jacea* exposed to medium O_3 concentration in open atmosphere are reported to have 50–70% more ascorbic acid in NC-R as compared to NC-S (Severino et al. 2007). The concentration of whole apoplastic ascorbic acid correlates directly with ozone tolerance in various floral species (Castagna and Ranieri 2009). However, higher ascorbic acid pool in sensitive varieties has also been shown in rice (Rai and Agrawal 2008) and wheat (Sarkar et al. 2010; Feng et al. 2010). D'Haese et al. (2005) reported that apoplastic ascorbic acid is not an important factor for differential O_3 tolerance of *Trifolium* clones.

Padu et al. (2005) showed that ascorbate concentration in *Betula pendula* did not rise significantly after got exposed by ozone even when stomata were fully open and O_3 flux to the mesophyll cells was showing higher increments. Statistically insignificant observations were noted for the total ascorbate and total dehydroascorbate level when *Pinus canariensis* was exposed to double the level of outdoor O_3 concentration (67 ppb). Hofer et al. (2008) observed that ascorbate content was reduced in needle extract of *Picea abies* in the presence of twice the level of ambient O_3 concentrations. *Poa* plants in monoculture as compared to *Vernonia* noticed a reduction in ascorbic acid content by 21.3 and 12.4%, respectively (Scebba et al. 2006). Iglesias et al. (2006) exposed *Clementina mandarin* cv. Marisol for 12 months under the presence of 30 and 65 ppb O_3 concentrations and found a decrease in foliar ascorbate pool.

Exposure to high levels of ozone results in increase in concentrations of SOD, APX, CAT, POD and GR in wheat (Chen and Gallie 2005; Sarkar et al. 2010), rice (Rai and Agrawal 2008; Wang et al. 2013; Sarkar et al. 2015), maize (Singh et al. 2014b) and mung bean (Mishra and Agrawal 2015). Tree species have also shown alterations in their enzymatic activities after exposing them with high levels of ozone concentrations. Activities of POD, CAT, APX and MDHAR were found to be elevated in *Liriodendron tulipifera* under high exposure to ozone (Ryang et al. 2009). Significant high values were reported in the activities of various defence enzymes like SOD, CAT, APX, DHAR, MDHAR and GR, in case of *Ginkgo biloba* (Lu et al. 2009; Feng et al. 2011).

Sensitive variety of rice also reported less concentration in SOD activity relative to tolerant variety under elevated O_3 (Rai and Agrawal 2008), but it did not differ between the filtered air and O_3-polluted environment in *Psidium guajava* (Pina and Moraes 2010). SOD levels rise significantly due to O_3 exposure in *Quercus mongolica* (Yan et al. 2010) and a sensitive birch clone (Toumainen et al. 1996). Biswas et al. (2008) claimed that there was a mean increase of 46% in POD activity in 20 wheat varieties at 85 ppb O_3 levels exposed for 7 h day^{-1} for 21 days relative to filtered air. Rai et al. (2007) and Rai and Agrawal (2014) also observed elevated POD activity in wheat species in the presence of natural ozone in the atmosphere relative to filtered air. POD activity was also reported to increase by 54.4 and 11.6% in *Achillea* and *Vernonia*, respectively, while it has also been reduced by 21.5 and 27.7% when grown in monoculture (Scebba et al. 2006). Progression in GR activity was very much higher in a sensitive birch clone (Toumainen et al. 1996). In *Fagus sylvatica*, exposed to double the atmospheric O_3 concentrations, glutathione content was significantly enhanced in seedlings as well as in mature trees relative to ambient levels (Herbinger et al. 2005). Rise in total and oxidized glutathione pool was also recorded in *Pinus canariensis* when exposed to 67 ppb O_3 levels (Then et al. 2009). Similarly, APX activity recorded in a resistant white clover clone compared to a sensitive one was found to be high, indicating its possible role in producing higher tolerance towards O_3 stress (Nali et al. 2005).

Significant variations in the antioxidant activity are very much connected with the differential O_3 sensitivity in various plants. Caregnato et al. (2013) have observed that changes in O_3 sensitivity between the two varieties of *Phaseolus vulgaris* depended on the variations reported in maintenance of intracellular redox homeostasis. SoyFACE study performed by Betzelberger et al. (2010) showed cultivar variations in the antioxidant activities of 10 soybean cultivars and suggested that antioxidant activity negatively correlated with photosynthesis and seed yield, therefore suggesting a trade-off between antioxidant system and carbon accumulation. Zhang et al. (2012) also observed variations in the total antioxidant activity of two deciduous (*Liriodendron chinense* and *Liquidambar formosana*) and six evergreen tree species (*Cinnamomum camphora*, *Cyclobalanopsis glauca*, *Schima superb*, *Ilex integra*, *Photinia* × *fraseri*, *Neolitsea sericea*) and observed lowest value in *Liriodendron chinense* and highest in *Schima superb* contributing to their difference in susceptibility towards O_3.

4.5.2 Characterization of Ozone Exposure

To summarize relation of ozone exposure to its impacts, it is mandatory to analyse concentrations averaged over 1 h intervals in a systematic and logical way. This acts as a substitute for dose (Aamlid et al. 2000). In specific, the exposure index is interrelated with the concept of effective dose (Alscher and Amthor 1988), i.e. it must collect and analyse the characteristics of exposure that is mostly connected with the amount of ozone absorbed by vegetation. Ozone uptake could be determined by multiplying the concentration near the leaf surface by the leaf conductance for ozone, and the absorbed dose would then be the main component of the flux rate over time (Bassin et al. 2007). This concept can be taken into consideration while analysing conductivity of the atmosphere (Feng et al. 2008a). Under controlled conditions of uniform air mixing, the diurnal pattern of ozone flux is analysed by leaf conductance and ozone concentration. Due to the lack of leaf conductance observations, radiation can be used as a substitute for leaf conductance which is presently used in agricultural farms/fields (Forster et al. 2007), and the most easy way is to use the measured ozone concentrations during daylight hours (e.g. >50 W/m^2 global radiation) to characterize exposure. In the case of those plant species which are having considerable leaf conductance during night, nevertheless, no such distinction could be made. The factors like atmospheric humidity, soil water availability and temperature are also responsible for affecting leaf conductance; however, these factors have not been taken into account to identify ozone uptake mechanism or chronic dose-related experiments. Chronic exposure to ozone can give rise to growth and yield loss. Consequently, the most appropriate exposure indices are related to chronic effects, and they are cumulative, i.e. they integrate exposure over time. Chronic impacts signify the arithmetic mean over the growing season of the daily average concentrations during specific time period, i.e. 7 h on daily basis (usually 09.00–16.00 h). The application of average concentration in a specific period of time implies equal weight to all concentrations. Nevertheless, controlled chamber dose-response studies of ozone suggests that only the intermittent exposure due to higher concentrations are responsible for causing chronic impacts (Heagle et al. 1999). This can be supported by the fact that more tolerant plant could able to detoxify ozone and other oxidants; if the concentration or the flux of ozone crosses the permissible limit, then harmful effect can occur. In order to calculate the cumulative exposure index, the significant variations between the actual hourly average concentration and the threshold concentration are then summed for the total exposure period (Karlsson et al. 2003).

Ozone is known for producing deleterious impact on plant species, and this concept was adopted at the United Nations Economic Commission for Europe workshop at Egham in 1992, when a permissible limit concentration of 40 ppb was suggested (UNECE 2010). Such exposure index is called AOT40, i.e. accumulated ozone exposure above a permissible limit concentration of 40 ppb, expressed in units of ppb/hour or ppm/hour. Statistical analysis of crop production data from European open-top chamber experiments has clearly noted that the use of this permissible limit normally provides better linear fits to exposure-response data as compared to the use of higher permissible limits (2005). A linear exposure-response relationship showed a better statistical basis for introducing critical levels adjacent to a specific effect as compared to other types of exposure-response relationship (Utriainen and Holopainen 2001). The application of threshold value of 40 ppb has been dominated over lower threshold concentrations because, in Europe, it widely corresponds to the boundary between average concentrations at those sites that possess low and high frequencies of photochemical events. However, the selection of this threshold does not involve the values less than 40 ppb, and those are having no effect on plant metabolism (Paoletti et al. 2010). Therefore, threshold values do not show a threshold for impacts, instead serve as marginal concentration. As the overall concentrations of ozone get increased with increased height in the atmosphere, the application of marginal concentration of 40 ppb does not suit for higher elevations. This index would be estimated by determination of concentrations during daylight hours only because only less rates of ozone deposition were measured over agricultural crops and forests during night hours (Lefohn et al. 1997). Though, it should be reported that in well-mixed fumigation chambers, extensive O_3 accumulation in trees can occur. Based on a typical exposure duration, the AOT40 is calculated for crops over 3 months (e.g. May–July) and for forest trees over 6 months (April–September).

4.5.3 Ozone Deposition Mechanism

Ozone deposition constitutes various mechanisms which can be described at different levels of resolution (Jonson et al. 2006). One aspect solely focuses on atmospheric mechanisms above the plant canopy, which are affected by wind turbulence and the unsymmetrical terrestrial landscape, including altitude and kind of vegetation. The another aspect that is very much common in ozone dose-response studies focuses on the role of individual leaf; ozone is deposited to vegetation canopies through uptake by leaves, majorly by stomata. The finest scale of resolution is noted by the reactions taking place inside the leaf. In forests, accumulation sites other than the stomata may also play a significant role in ozone deposition, for example, cuticles, bark, litter, soil and canopy air space, where ozone can be reduced by biogenic hydrocarbons or oxides of nitrogen released from organic decomposition in the soil or by the foliage (Grini et al. 2005).

The degree of gas exchange occurs through the stomatal pores, i.e. the ozone flux, related to the total pore area per unit leaf area, and pore density. Mostly plants possess pore area which consists of 0.5–1.5% of the leaf surface (Islam et al. 2000). The extent of pore opening and also the stomatal diffusion resistance depends on the internal environment of the plant. The main external factors are light, temperature, humidity, water supply, wind speed and altitude, whereas the internal factors consists of the partial pressure of carbon dioxide in the intercellular system, the content of water and ions in the tissues and plant growth regulators (gibberellic acid and cytokinin responsible for opening and abscisic acid promotes closing). Ozone uptake by crops in highly extreme environments is very much connected with stomatal conductance and also follows the diurnal pattern of radiation (Gravano et al. 2004), whereas, under less extreme environment, the canopy can be decoupled from the atmosphere, and ozone deposition depends mainly on air mass movement over less control exerted by stomata. Due to difference in canopy structure and different atmospheric conditions, the flux or deposition of ozone mainly depends on leaf conductance (Fiala et al. 2003). In case of ozone uptake, the particular leaf area is measured on the basis of dry weight of the leaf (i.e. the area of assimilatory leaf material per unit dry weight), and this has been reported as the major determining factor. Monitoring at different levels using branch cuvettes on spruce trees reported that the extent of ozone deposition velocity varies between high- and low-elevation sites (Duenas et al. 2002; Bartholomay et al. 1997). Approximately during afternoon time, conductance increases with increasing altitude. Interestingly, it has been found that stomatal uptake of ozone may also occur at night in various coniferous tree species (Ashmore 2005). Nevertheless, due to lack of a considerable rate of ozone deposition in forests at night, accumulated exposure index (AOYT40) should be used. In the case of crops, AOT40 can only be applied during daylight hours.

4.5.4 Effects of Ozone on Physiology and Biochemistry of Plants

Ozone may affect the cell metabolism, individual organs, plant species, communities and ecosystems (Bytnerowicz et al. 2007). After making passage through the stomatal pore, O_3 can react with organic molecules (e.g. ethylene, isoprene) in the intercellular air space or with components of the extracellular fluid. While considering both the cases, secondary oxidants (e.g. primary ozonides, hydroxyhydroperoxides) may be formed, which in turn could react with the protein component of the cell membrane (Calatayud et al. 2011). This reaction is prohibited to some extent due to the presence of radical scavengers, such as ascorbic acid and polyamines (Coyle et al. 2002). Formaldehyde, formate and acetate are deposited in affected tissue, probably as a result of the reaction between ozone and ethylene or between O_3 and the phenylpropanoid residues of lignin. There are various reports which confirmed that ethylene formation determines the sensitivity of plants to O_3 (Eckmullner and Sterba 2000). Elevated concentrations of O_3 cause target cells to collapse, resulting into local visible tissue destruction. The effect on the plasma membrane can cause alterations in membrane functions which may affect the internal concentrations of ions (e.g. Ca^{2+}) (Larsen et al. 1990). Consequently, this causes the changes in the osmotic potential of the cytoplasm that will produce reduction in photosynthetic processes present in the chloroplasts. Decline in carbon dioxide fixation by the enzyme ribulosebisphosphate carboxylase is a special symptom found in leaves exposed to ozone over longer periods of time (Matyssek et al. 2008). Further, inhibition of carbon dioxide assimilation gives rise to direct or indirect inhibition of stomatal opening that reduces uptake (Nali et al., 2005). Stimulated dark respiration generally occurs together with reduced photosynthesis (Oksanen et al. 2004), most likely due to increased respiration linked with maintenance and repair (Peterson et al. 1999). The combined impacts of decreased assimilation and increased respiratory loss of carbon dioxide include a total reduction of assimilate production and export from the source leaves. In crop plants which are exposed with high levels of ozone for a longer duration, the phenomena of senescence get initiated, and enhanced catalysis results in rapid loss of protein and chlorophyll (Repo et al. 2004). As a consequence, the duration of positive net assimilation of carbon dioxide is lost, and the overall production of assimilates declines. Under conditions of decreased assimilate supply through photosynthesis, transfer of carbon to different organs may vary, leading to altered growth responses of these organs. Typically, higher priority is given to the shoot relative to roots and/or other storage organs (e.g. seeds). This results in reduced root-shoot weight ratios or in a reduction of the ratio between seed yield and total biomass production.

In agricultural crops, this results in reduced grain or seed yield (Ro-Poulsen et al. 1998).

4.5.4.1 Impact of Tropospheric Ozone on Pigment Content

Chronic exposures to low concentration of ozone which accommodates variation in pigmentation or bronzing, chlorosis and premature senescence result in visible injury. Visible foliar injury serves as a major evidence of the hazards faced by the plants due to ozone exposure. Thus, when visible foliar injury can be observed, damage has surely been caused to the plants. Acute exposures to higher ozone concentrations may result in flecking and stippling. In certain species a correlation is observed between visible injury and reduction in growth, for example, yellow poplar, loblolly pine and white pine, whereas according to many studies for a wide range of species, there does not appear to be a correlation. Some of the physiological impacts of ozone contact consist of reduced photosynthesis, amplified turnover of antioxidant system, injury to reproductive procedures, increased dark respiration, dropped carbon transport to roots, reduced decay of early successional communities and reduced forage eminence of C4 grasses. Reactions to ozone are considerably varied in species, but in certain cases results even varied for the same species. Other important variables that affect ozone, like visible injury, are photosynthesis (Duenas et al. 2002) and stomatal conductance (Eckmullner and Sterba 2000). Even if visible injury is not observed, it is not necessary that vital damage has not occurred in the plant due to contact with ozone. An example for this can be Scots pine which showed no sign of visible injury when it was grown in an environment exposed to ozone (Fowler et al. 1998). Also, studies have shown that in certain plants net carbon assimilation rate reduced along with the transpiration in the region of higher concentration without any damage to the leaves visible to the eye (Pleijel 2011). Studies have also shown that continuous ozone exposure resulted in reduction in total chlorophyll content, even though this phenomenon could not be detected by the naked eye. Thus, even in the presence of visible foliar damage, the plants are affected with regard to other variables too even if the naked eye cannot detect the symptoms.

4.5.4.2 Impact of Tropospheric Ozone on Starch Content

According to studies and various experiments, ozone is responsible for significantly reducing concentration of starch in stems, coarse roots and fine roots of nongrowing seedlings (Fowler et al. 1998; Pleijel 2011; Biswas et al. 2008; Broberg et al. 2015; Jonson et al. 2006; Grini et al. 2005; Islam et al. 2000; Gravano et al. 2004). The experimental observations have shown a reduction of 72% in fine starch in roots which decreased during the 4-week regrowth period which was not the case with concentrations found in the needles as they remained almost same. During the regrowth period, stem starch concentration was decreased by 65% in seedlings that were exposed to ozone, while the control seedlings saw a decrease of just 25%. Concentrations of glucose showed a little variation by tissue type and growth status in the nongrowing and growing seedlings. In the case of nongrowing seedlings, concentration of glucose was higher in the stems of seedlings that had been in contact with the ozone than the control seedlings. In the case of coarse roots, there was a significant reduction in glucose concentration due to ozone exposure, while the overall concentration came out to be low in the experimental results. In the case of growing seedlings, glucose concentration saw significant reduction in glucose concentration in coarse, fine and new roots. According to the experiments, this can be inferred seedlings having new roots had glucose concentration 21% of those of control seedlings as a result of exposure to the highest ozone regime. Experiments also showed that the needles had a high concentration of fructose and it was higher compared to any other part (Ro-Poulsen et al. 1998). Nongrowing seedlings showed greater concentration of stem fructose than the control seedlings. Fructose concentration underwent a decrease in fine roots and new roots in seedlings exposed to higher ozone regime compared to the control seedlings. In the case of sucrose, concentration showed wide variations in nongrowing ozone in presence of all levels of ozone and showed marginal significant ozone impacts in seedlings of the highest regime. Experiments showed that sucrose content was significantly lower in stems, coarse and fine roots of ozone-exposed seedlings compared to controls. Concentration of sucrose was lower in new roots of seedlings treated with ozone than the new roots of the control seedlings, even though the erraticism was very high and the significance of the results in the highest ozone treatment was marginal. Monosaccharides saw significant reduction in roots of growing seedlings due to past contact with ozone. In the case of nongrowing seedlings, ozone-treated plants saw higher stem concentration than the control plants. The new roots of growing seedlings experienced the greatest reduction in monosaccharides induced because of exposure to ozone as observed in the experiments (Bytnerowicz et al. 2007; Calatayud et al. 2011).

4.5.4.3 Impact on Proline Content

Proline is derived from various proteins and enzymes and has been significant in providing a source of energy and behaves as an osmoprotectant under stressed conditions. High proline concentrations under stressed conditions reduce the breakdown of other proteins (Oksanen et al. 2004). High rate of proline concentration imparts increase of tolerance against salinity and drought stress in various plant species (Pleijel 2011). Proline has the property to act as free radical scavenger which can protect plants against several damages because of oxidative stresses. Increased exposure of ozone to plant species makes chloroplasts highly susceptible to generate ROS and creates oxidative stress (IPCC 2014). Environmental stress can cause extra ROS which are cytotoxic to all organisms (Biswas et al. 2008). The harmful impacts of pollutants are caused by generation of ROS in plants, which produce peroxidative destruction of cellular constituents (Bytnerowicz et al. 2007). Therefore, increased proline in plants is regarded as an indicator of higher stress such as osmotic stress (Calatayud et al. 2011; Matyssek et al. 2008; Ro-Poulsen et al. 1998).

4.5.4.4 Enzymatic Profiles and Role of Antioxidants

(a) Superoxide dismutase: Signs of visible injury came to prominence after two or three pretreatments of the plants that were found to be in contact with high-level ozone. The visible symptoms that were observed included small areas of localized chlorosis and necrosis which in turn resulted in spots or flecked appearance to the adaxial surface of the leaf (Mills et al. 2007). With the inception of visible symptoms, the SOD levels saw a significant increase above the control values. Continuous low-level treatments have given results of chronic injury symptoms which can be related to the cumulative SOD activity in damaged plants over some time (Ali et al. 2012).

Experiments (with 9-day-old plants) have shown an increase in SOD activity by 21% in plants treated with ozone as compared to the control plants. On comparing the SOD activities in plants that were undergoing acute fumigation after emergence to those that remained in ozone-free air, it was observed that there were clear indications of enzyme induction after visible injury that became clearly noticeable. The small but significant increase in SOD activity after little exposure was not followed by significant injury, but this inconsistency can be credited to the absence of sensitivity of %LAN assessment at lower injury levels (Zhao et al. 2009; Tang et al. 2013; Wang et al. 2013).

In the case when experiments were conducted using 2-day-old plants, no changes in levels of minor injury or SOD activity was observed until the third day of experiment. These results signified that injury was responsible for enzyme induction and not the ozone (Calatayud et al. 2011; Matyssek et al. 2008; Oksanen et al. 2004; Ro-Poulsen et al. 1998; Creissen et al. 1999; Zheng et al. 2000).

Considering the case of kidney beans, manganese SOD activity is accountable for 25% to 37% of the total activity, and this is largely related to mitochondria 1 fraction. On the basis of sensitivity to cyanide, this type of SOD and cuprozinc type can be distinguished. Thus, while considering the experiments, pretreatment with low ozone showed no significant impact on total extracted SOD activity even though it was expected that exposure to ozone might cause alteration in the ratio of cuprozinc-manganese SOD. Experimental observation also show that the young leaves are predominated by cuprozinc SOD and later the manganese form begins to take control. This can be now inferred from the present studies that increased levels of SOD only occur with the beginning of or just after the appearance of visible symptoms of damage, whether caused due to repetitive exposures to low levels or by small doses of ozone (Duenas et al. 2002).

Hence, it can be suggested that SOD plays a secondary role in response of leaves to ozone pollution after the damage has occurred. Also, it is not sure that enhanced SOD activity is significant to protect against small ozone exposures as the experimental observation also showed that the damage continued to increase with each exposure in spite of the substantial increase in levels of SOD. Also, no evidence was found to support the observation that susceptibility of the primary leaves to small doses of ozone reduced was caused by pretreatment with subacute doses and has any relation with SOD introduction (Grini et al. 2005).

(b) Ascorbic acid: Ascorbic acid resides in the apoplast and is the possible hunter of ROS that could weaken ozone injury. Ascorbic acid is transported to the apoplast of the leaf after being synthesized in the cell. Many authors suggest that ascorbic acid plays an important role in many cell wall processes. Ascorbic acid is known to hunt ROS and react with ozone to lessen the chance of damage caused due to ozone and also acts as a substrate in enzymatic reactions that hunt ROS (Creissen et al. 1999). Ascorbate biological synthesis and transport have been occupied in cell wall biosynthesis and signalling. Apoplastic ascorbic acid is suggested by several studies to be oxidized when in contact with the ozone, which results in formation of dehydroascorbic acid (DHA), which is then transferred back into the cytoplasm where the coupled reactions consist of DHA reductase and reduced glutathione reduces it to ascorbic acid. Involvement of extracellular AA in ozone detoxification processes is suggested by apoplastic AA concentration and change in redox status in response to ozone. Snap bean and *Plantago major* are found to be sensitive to ozone which can be correlated with concentration of extracellular AA (Zheng et al. 2000). *Arabidopsis thaliana* mutants have low foliar concentration of AA (vtc1) and exhibit hypersensitivity to ozone. Transgenic tobacco (*Nicotiana tabacum* L.) plants have changed expression of DHA reductase and exhibit variation in leaf AA concentrations which positively correlate with their tolerance to ozone (Chen and Gallie 2005). However certain studies have questioned the efficiency of AA in protecting the plants against damage by ozone as the apoplastic concentration are not sufficient enough for effective detoxification of ROS. Also, the differential ozone sensitivity of NC-S and NC-R clover clones was not found to be associated with apoplastic AA concentrations (D'Haese et al. 2005). So there are still quite a few mysteries that need to be solved regarding the processes involved in maintaining the plant health with relation to ozone.

(c) <u>Glutathione:</u> Glutathione is one of the effective and essential intracellular hunters whose role as an antioxidant can only be maintained when GSSG is reduced to GSH through GR activity. Glutathione pool had a considerable effect of ozone treatment as shown by the experiments. The GSH-(GSH+GSSG) ratio dropped noticeably with an increase in the oxidized form and decrease in the reduced form. Stress conditions are actually responsible for the increase in GSSG content. Another observation that can be made from the experiment results is that it seems that the GR activity has no impact on the stable state levels of glutathione. The relative rate of synthesis and degradation is related to the growth conditions, leaf age and NADPH level that seem to be the main factors that help in calculating the total content of glutathione in leaves and is not related to recycling of GSSG via GR activity. GR activity saw a slight stimulation in mature leaves 24 h post fumigation. The increase in the GR activity is not usually more than double (Oksanen et al. 2004) under the stress conditions, sometimes no increase is observed, and at others a drop is observed (Creissen et al. 1999) which suggests that variation in GR isoform population and not changes in total activity is of primary importance. It is not necessary that GR activity is in the steady-state levels of GR protein in response to environmental stresses. The experiments have shown small changes in the GR activity, and protein levels recorded after ozone disinfection, regardless of strident fall in specific mRNA level, were observed. This may signify that the enzyme is more stable than other proteins (Chen and Gallie 2005). The sudden decrease in GR mRNA is shown by a higher turnover of mRNA or specific gene down instruction which is encouraged directly by active oxygen species or by messengers like jasmonic acid, salicylic acid or ethylene (Calatayud et al. 2011).

4.5.5 Impact of Tropospheric Ozone on Photosynthetic Rate, Stomatal Conductance and Photosynthetic Output Rate

High doses of ozone cause stomatal closure because of damage to epidermal cells. The passage of ozone in leaf by stomata ahead to mesophyll cells gets dissolved in the aqueous layer of apoplast to generate ROS such as H_2O_2, hydroxyl radical, peroxyl radical and superoxide radicals (Felzer et al. 2007). Stomatal closure due to exposure to ozone is responsible for reduction in stomatal conductance (Gravano et al. 2004; Creissen et al. 1999; Felzer et al. 2007). Reactive oxygen species cause damage to plasma membrane via lipid peroxidation by producing alterations in membrane permeability, fluidity, potassium (K^+) exchange via ATPase reactions and calcium (Ca^{2+}) exclusion (Islam et al. 2000). Free radicals resided in the guard cells damage the chloroplast membranes, and consequently the photosynthetic apparatus would be damaged. Swelling of thylakoids, rise in plastoglobuli per chloroplast and injury of membranes lead to leakage of ions and resulted in photosynthetic capacity (Plazek et al. 2001). Mesophyll cell are affected directly or indirectly by release of organic and inorganic solutes. The stomatal closure can result in decreased production of energy equivalents like ATP and NADPH and are responsible for limiting the dark reactions of the photosynthesis.

Quantum yield (ΦPSII) and photochemical quenching (qP) are significantly reduced, whereas non-photochemical quenching (NPQ) rises in the leaves of plants exposed to O_3 (Plazek et al. 2001). High qN with successive decrease in qP indicates non-radiative dissipation of energy. The loss of quantum yield of ET is directly related to downregulation of PET. The reduction of photochemical efficiency (F*v*/Fm) denotes damage to PSII reaction centres (Matyssek et al. 2008; Ro-Poulsen et al. 1998; Creissen et al. 1999; Zheng et al. 2000; Chen and Gallie 2005; D'Haese et al. 2005; Felzer et al. 2007). Increase in Fo indicates alteration in the transport of excitation energy from light-harvesting complexes to reaction centres. In the light reactions, the generation of electrons by the water splitting reaction in PSII is impaired, and electron transport from PSII to PSI is lost.

The stomatal closure reduces the rate of CO2 assimilation but increases the diffusive resistance of CO_2 in the mesophyll, thus changing the allocation of carbon to different parts of plant species (Fowler et al. 1998; Grini et al. 2005; Chen and Gallie 2005). The reduction in the carboxylation efficiency affects the light and dark reactions of photosynthesis (Pleijel 2011; Grini et al. 2005; Matyssek et al. 2008). The harmful effects on the carboxylation efficiency showed direct oxidative damage and indirect heat-related injuries to RuBisCO. Stomatal closure may be the first mechanism for plant protection against the harmful impacts of O_3. On the other side, increased production of antioxidants has shown to curb oxidative stress induced by gaseous pollutants. A decline in RuBisCO activity majorly contributed to the degradation of photosynthetic capacity of plants (Calatayud et al. 2011; Creissen et al. 1999).

Decline in chlorophyll concentrations gives rise to decline in light harvesting and total assimilation rate. The reduction in the light-harvesting capacity of chlorophyll together with a decreased efficiency of photosynthetic energy conversion results in decreased total assimilation. Potassium flux changes the guard cell volume in the stomata and regulates the stomatal aperture. Elevated ozone exposure inhibits the activity of guard cell K^+ channels, which intervene stomatal opening and leads to reduced photosynthesis (Hassan and Tewfik 2006).

Non-stomatal factors which impact the photosynthetic efficiency include (i) lesser RuBP regeneration from lower pools of Calvin cycle intermediates, (ii) reduced efficiency of RuBisCO because of direct enzyme oxidation and (iii) reduced carbon dioxide transport to the enzymes. Ozone induces decline at RNA transcript level for the small subunit (rbcS) and large (rbcL) subunits of RuBisCO (Zheng et al. 2000). It also decreases the expression of photosynthetic genes for RuBisCO activase (Meehl et al. 2007; Duenas et al. 2002).

Pigments like zeaxanthin also intervene photoprotection in O_3-exposed plant species. Antioxidant enzymes like ascorbate peroxidase cause detoxification of H_2O_2 by breaking up into simpler substances like water through a number of reactions in the ascorbate-glutathione cycle (Bartholomay et al. 1997). Antioxidants like hydrophilous ascorbate (vitamin C) and lipophilous α-tocopherol (vitamin E) protect the plasma membranes of plant species. Ascorbic acid acts an important role in defending against ROS in plants (Fowler et al. 1998; Pleijel 2011; Biswas et al. 2008). The biological synthesis of phenylpropanoids increases more in sensitive species as compared to the tolerant ones. The decrease in carbon assimilation of plants exposed with O_3 increases the PAL activity which is meant for the production of phenylalanine and transcinnamic acid and precursor of phenylpropanoids. Polyamines protect plastids and thylakoid membranes against O_3 high concentrations. Addition of external polyamines decreases damage caused by O_3 in plants. These polyamines are also related with thylakoid membranes and a number of photosynthetic subcomplexes. They will further conjugate with hydroxycinnamic acids and protect the photosynthetic machinery from ROS activity (Gravano et al. 2004). A decrease in thylakoid-bound is significantly responsible for rise of antenna size of the LHCII; however, the number of reaction centres per unit area plus the maximal photosynthetic rate and the maximum yield of photochemistry (Fv/Fm) decreased. The protections by polyamines against oxidants include (i) scavenging of ROS, (ii) increasing the infiltration rate of antioxidant by SOD enzyme, (iii) protecting the membranes against oxidant damage, (iv) altering the redox state of the cells and (v) maintaining the expression of genes. Isoprene washes out ROS and provides protection against oxidative stress (Lal et al. 2000). It effectively reacts with O_3 that produces hydroxymethyl hydroperoxide, hence aggravating the O_3-induced damage. It reduces O_3 by directly reacting with it in the intercellular spaces and, therefore, counteracts the O_3 damaging impact on membranes (Creissen et al. 1999; Felzer et al. 2007). Rise in flavonoid content in plants treated with O_3 suggests their role in washing out ROS that consists of superoxide anion, hydrogen peroxide and hydroxyl radical. They also play a role in peroxidase-mediated catabolism of H_2O.

4.5.5.1 Photosynthetic Pigments

Ozone-produced ROS are known to change the membrane-bound organelles, like chloroplast, that resulted in destruction of photosynthetic pigments (Grini et al. 2005; Eckmullner and Sterba 2000). Significant decline in total chlorophyll content of rice plants under ambient and elevated dose of O_3 of 27 and 44%, respectively, was recorded (Gravano et al. 2004; Duenas et al. 2002; Bartholomay et al. 1997; Bytnerowicz et al. 2007; Calatayud et al. 2011; Eckmullner and Sterba 2000). Feng et al. (2008) documented that about 40% decline in chlorophyll content in wheat plants under O_3 exposure was reported in their meta-analytical study.

High concentrations of O_3 showed decreased trend in total chlorophyll content in subtropical broad-leaved tree species like *Cinnamomum camphora*, *Cyclobalanopis glauca* (Ali et al. 2012) and *Citrus clementina*. Gielen et al. (2007) treated *Fagus sylvatica* to double the times of ambient ozone concentration and recorded 15.9% decline in total chlorophyll content. Riikonen et al. (2005) reported 5 and 19% decreased trend in total chlorophyll content in two European silver birch clones 4 and 80, respectively, upon ozone exposure. In six species of *Trifolium alexandrinum* cultivars, total chlorophyll showed decreased trend, ranging from 13.1 to 57.3% and carotenoids by 9.4–39.2% under ozone treatment exposed with a dose of 10ppb (Chaudhary and Agrawal 2015; Leitao et al. 2007). *Pinus canariensis* treated with high O_3 concentration (67 ppb) showed an increment of 14.3% in photosynthetic pigments (D'Haese et al. 2005). In *Vernonia* also, O_3 exposure increased the total chlorophyll content (Plazek et al. 2001).

Carotenoids are vital photoprotective agents that prevent photooxidative chlorophyll destruction (Felzer et al. 2007; Plazek et al. 2001; Gielen et al. 2007; Riikonen et al. 2005). Variations in carotenoid content after exposing them with O_3 may result in modification in their capacity to protect photosystem against photooxidation. Several studies have reported O_3-induced decline (Calatayud et al. 2011; Eckmullner and Sterba 2000; Matyssek et al. 2008; Ro-Poulsen et al. 1998; Creissen et al. 1999; Zheng et al. 2000; Chen and Gallie 2005; Felzer et al. 2007) or induction (Bartholomay et al. 1997; Bytnerowicz et al. 2007; Calatayud et al. 2011) in carotenoid content. The effects of O_3 on 3-year-old *Clementina mandarin* trees were reported at two O_3 concentrations, and decline in total chlorophyll as well as carotenoid pools in leaves was recorded (Islam et al. 2000; Gravano et al. 2004; Duenas et al. 2002; Bartholomay et al. 1997).

4.5.5.2 RuBisCO Content

The decrease in RuBisCO content after exposing them with O_3 has a direct effect in form of significant decline in photosynthetic capacity (Leitao et al. 2007). Ozone-induced decrease in RuBisCO quantity may probably be due to inhibition of synthesis and/or its elevated degradation (Gielen et al. 2007). Sarkar and Agrawal

(2010a) observed that high O_3 caused damage to large subunit (LSU) and small subunit (SSU) of RuBisCO in rice. Same results were obtained in wheat (Sarkar and Agrawal 2010a, b), maize (Ma et al. 2016) and mung bean (Li et al. 2014). Amount of RuBisCO increased by 10, 20 and 17% and decreased by 7% in O_3 atmospheres of +20, +40, +60 and +80, respectively, compared to nonfiltered chambers (Leitao et al. 2007).

4.6 Conclusion

The present chapter focuses on the significance of secondary criteria air pollutant, i.e. tropospheric ozone both at international and national level. Relatively, developing countries are more prone to tropospheric ozone pollution due to high anthropogenic activities. As tropospheric ozone is secondary product due to reactions among precursors like NO_2, VOCs and CO in the presence of sunlight, therefore its chemistry is a challenging aspect. Increasing concentrations of ozone leads to climate change due to its major role in greenhouse effect. In the case of human health, major observations show a strong relationship between short-term exposure and pulmonary dysfunctions, pulmonary inflammation and other lung disorders along with indications of pain and cough on deep inspiration, immune system energization and epithelial cell injury. Ozone exposure studies also lead to permanent damage. Epidemiological studies conducted on broad scale with respect to communities or analysing real-time series of daily environmental and health data reflects a stable and clear relation between ozone and immediate and short-term adverse health impacts, expressed in terms of death rate or morbidity indicators. In the case of plants, tropospheric ozone is the most dangerous pollutant that is why it is called as phytotoxic agent. Ozone causes visible injury, impairs photosynthesis, alters stomatal conductance, reduces yield and also disrupts the metabolic pathway of crop plant species. Ozone also increases the susceptibility of crop plants towards pest and diseases. Hence, overall, this secondary criteria air pollutant needs a stringent check on its concentrations, and there is an urgent call for agricultural scientists, policymakers and farmers to work together for the betterment of environmental safety, food security and sustainability and overall maintenance of ecological balance.

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