Journal of Scientific Research
Banaras Hindu University, Varanasi

Vol. 55, 2011 : 77-102
ISSN : 0447-9483

GASEOUS AIR POLLUTANTS : A REVIEW ON CURRENT AND FUTURE TRENDS OF EMISSIONS AND IMPACT ON AGRICULTURE

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ABSTRACT

Air pollution recieves one of the prime concern in India, primarily due to rapid economic growth, industrialization and urbanization with associated increase in energy demands. Lacks of implementation of environmental regulations are contributing to the bad air quality of most of the Indian cities. Air pollutants produced in any air shed are not completely confined, but at time trespassing all the geographical boundaries, hence donot remain only a problem of urban centres, but spread and affect remote rural areas supporting large productive agricultural land.

Air pollutants pose risks on yield of crops depending on the emission pattern, atmospheric transport and leaf uptake and on the plant's biochemical defense capacity. Recent trends have shown decrease in SO_2 emissions, but increase in NO_2 emission due to more number of automobiles. In past few decades, tropospheric O_3 has been identified as a most important air pollutant of rural areas. Air pollutants produce reactive oxygen species (ROS), which adversely affect biochemical processes of plants and reduce their tolerance capacity to other stresses also. Several vital physiological processes such as photosynthetic CO_2 fixation and energy metabolism are also affected negatively by air pollutants. An adverse effect caused by air pollutants depends not only upon its concentration, but also on the duration and combination of air pollutants. The present review deals with present and future trends of major gaseous pollutants emissions and their impact on crop performance.

Keywords : SO_2, NOx, O_3, ROS, crops

1. Introduction

The natural resources have been exploited by the man for meeting his needs from the dawn of civilization. However, the acceleration of exploitation has been increasing at a high rate and in non-judicious manner during past few decades especially with the advent of industrial revolution. Industrialization has provided humanity with materials and social benefits. It has also brought in its wake up many unwanted substances and social problems. One of these problems is the degradation of the environment. These environmental problems are becoming threats to the very existence of the living beings. The environment upon which our life is most dependent, has fallen victim of pollution brought by man himself through unplanned and unscientific urbanization, industrialization and mineral exploitation.

Literally environment means surrounding. Environment influences all aspects of life. Until the conference on Human Environment held at Stockholm in 1972, the importance of environmental protection for improving the standard of living of human being was not realized. In 1991 at the World Commission on Environment held at Rio De Janeiro, the Heads of different countries met and decided to take immediate action to improve the Global Environment.

Air pollution has become an extremely serious problem for the modern industrialized world. Air pollution may be defined as any atmospheric condition in which certain substances are present in such concentrations that may produce undesirable effects on man and ecosystem. These substances include gases (sulphur dioxide, nitrogen oxides, carbon monoxides, hydrocarbons, etc.), particulate matters (smoke, dust, fumes, aerosols, etc), radioactive materials and many others. Air pollution may or will have harmful effects on living things and materials. It may interfere with biochemical and physiological processes of plants to an extent, which ultimately leads to yield losses (Heck et al., 1988).

Air pollution was earlier considered as a local problem around large point sources. But due to use of tall stacks and long range transport of pollutants, it has become a regional problem. The transboundary nature of pollutants was clearly evident when areas remote from sources of air pollution also showed higher concentrations of air pollutants. Uncontrolled use of fossil fuels in industries and transport sectors has led to the increase in concentrations of gaseous pollutants such as SO_2, NOx, etc.

Many developing countries including India have experienced a progressive degradation in air quality as a result of rapid pace of development over the last three decades. During this period newly industrialized countries underwent unparallel economic growth, swelling urban populations and generated excessive emissions from automobiles, factories and refuse burning (World Bank, 1996). Much of the 20th century witnessed an increasing trend in urbanization in developing countries. While urbanization can be a stimulus of development, in the process many cities in Asia, Africa, the Near East and Latin America are facing two challenges of pollution and congestion (Ashmore, 2005). In 1960, less than 22% of developing world's population was urban and the proportion increased to 34% by 1990. The projections are that 50% of the global population will be urban by 2020. The general state of the environment, including air quality, is deteriorating in many cities of the developing countries. World Bank studies in selected cities of developing countries have shown that swelling urban populations and the growth of industrial activities and automative traffic in Asia have caused serious air pollution (World Bank, 2009).

The chemical composition of the atmosphere is being altered/changed by the addition of gases, particulates and volatiles substances, which may be toxic to living beings. The levels of air pollutants are rapidly increasing in urban, periurban and rural areas in many megacities (urban population greater than 10 million) of the developing world (Agrawal, 2005). The adverse effects of air pollution have been associated with three major sources: sulphur dioxide and solid particulates from fossil fuels; photochemical oxidants and carbon monoxide from motor vehicles and miscellaneous pollutants such as hydrogen sulphide, lead and cadmium emitted by smelters, refineries, manufacturing plants and vehicles (Birley and Lock, 1999). Increased numbers of motor vehicles, power generation, domestic fuel use, refuse burning and other miscellaneous sources contribute to the problem of urban air pollution in India. The fossil fuel consumption has increased from 75 million tonnes per year in 1964 to 245 million tones per year in 1990 (Shrestha et al., 1996). The records of Ministry of surface transport in India show that the numbers of vehicles in the country was 21.3, 53 and 67 million in 1991, 2000 and 2003, respectively. In urban areas, the main sources of air pollution are power plants, industries, motor vehicles and domestic sources. While industrial air pollution is localized, mobile sources have emerged as the most significant contributor to regional air pollution.

Until 1980, air pollution was primarily the problem of urban and industrial regions in India. But in the last two decades, due to changes in pattern of air pollutant emissions, greater pollutant impacts have also been experienced even in rural and more remote areas. A high rate of economic growth in India has resulted in mass scale influx to urban areas thus increasing the urban population. Urban air pollution has a direct impact on periurban agriculture as pollutants disperse in all directions along the wind. During transportation a variety of reactions occur among primary pollutants to form secondary pollutants causing greater adverse effect in periurban areas. In Indian cities concentrations of phytotoxic air pollutants often exceed the toxic limits (Trivedi et al., 2003; CPCB, 2009). Rapidly growing cities, more traffic on roads, use of dirtier fuels, reliance on outdated industrial processes, growing energy consumption, and lack of industrial zoning and environmental regulations are all contributing to the bad urban air quality and deteriorating public health.

Keeping in view the information that urban air pollution may be a serious threat to agricultural productivity in areas around urban centers and there exist variations in pattern of pollutants due to interactions during transport, the present review focuses on the trend of emissions and concentrations of major gaseous pollutants, SO_2, NO_2 and secondary pollutant O_3 and their effects on agricultural crops.

2. Past and Present trends of air pollutants

In India, the problem of air pollution has assumed serious proportions in most of the major metropolitan cities, where vehicular emissions contributed about 72% and industrial emissions about 20% to the ambient air pollution (Garg et al., 2001).

Sulphur dioxides (SO_2)

Anthropogenic SO_2 emissions have been increasing by about 4% annually. This trend parallels with rise in global energy consumption. SO_2 emissions have reduced in most of the developed and developing countries due to stringent pollution control measures. Industrial sources, thermal power plants and transport sectors are identified as sole contributors for SO_2 emissions. In Delhi, thermal power plants and other industrial sources are responsible for most of the SO_2 emissions. Increase in SO_2 emissions are also linked with increase in motor vehicle population (Gurjar et al., 2004).Between 1970 and 1980, there was 66% increase in SO_2 emission, thereafter the increase declined due to introduction of natural gas as one of the fuel source.

Total SO_2 emission shows a decreasing trend since 1980. SO_2 emission decreased by 53% from 1990-2006 (US EPA, 2007). United States Environmental Protection Agency reported that annual SO_2 emission was 31.2 and 15.8 million tones in 1970 and 2003, respectively (US EPA, 2007). According to the RAINS estimates, the world emissions of SO_2 in 1990 were about 120 million tons, while in 2000, the emissions were about 20% lower than 1990 level. Current energy and air pollution control policies cause a further 5% decrease till 2010- 2020 (Cofala et al., 2007)

Many of the metropolitan cities in India are ranked amongst the top few cities of the world for air pollutants concentrations (Baldasano et al., 2003). The analysis of National Environmental Engineering Research Institute (NEERI), India air quality data in 1990 for annual average of SO_2 concentrations reveals a trend for increasing concentrations (from 3.8 to 15.2 ppb) in most of the parts of northern region, except for a few cities including Delhi, that had mean annual SO_2 concentration above 22.8 ppb after 1985 (Agarwal et al., 1999). In 2009, scenario has changed as SO_2 concentration has declined throughout the country with concentrations varying between 1.5- 13.7 ppb. Among metropolitan cities SO_2 concentrations in Delhi, Mumbai, Chennai and Kolkata were 2.3, 2.3, 3.4 and 6.1 ppb, respectively (ENVIS, 2010). Studies conducted in Varanasi city during 1999-2001 showed that SO_2 concentration ranged from 5.32 – 5.5 ppb (Trivedi et al., 2003). National ambient air quality standard given by Central Pollution Control Board (CPCB) in India is given in Table 1.

Nitrogen oxides (NOx)

Nitrogen dioxide (NO_2), a highly reactive gas is formed in the ambient air through the oxidation of nitric oxide (NO). Nitrogen oxides occur in atmosphere naturally and as a result of human activities. Nitrogen oxides are formed mainly by the burning of fossil fuels. This results from a chemical reaction between atmospheric N_2 and O_2 in the presence of heat to form NO, which then reacts again with O_2 to form NO_2. The rate of reaction is determined by the temperature of combustion. Thus, unlike SO_2, NO_2 is not a component of fossil fuel, but results from a catalytic reaction of heat with atmospheric N_2 and O_2 in the combustion process.

Anthropogenic emissions of NOx lead to majority of all nitrogen inputs to the environment. The major sources of anthropogenic NOx emissions are automobiles and power plants. Mobile sources such as automobiles contributed 58% and stationary point sources such as industries and power plants accounted for 32% of NOx emissions in USA (HARC, 2008). In most recent State Implementation Programme report, total regional NOx emissions for 2008 was estimated to be approximately 548 tones day^{-1} which has reduced from 831 tones day^{-1} in 2002 (HARC, 2008). In USA, NO_2 emission increased upto 1997, after which a steady decrease has been established. US EPA showed that annual NO_2 concentration decreased by 30% from 1990 to 2006 (US EPA, 2007). During 2002, at all the monitoring stations in USA, concentrations of NO_2 were within the limit of prescribed standards set by National Ambient Air Quality Assessment Standard (NAAQS). In China, number of vehicles has increased by six fold since 1980 (Liu and Diamond, 2005), resulting in rise of NOx concentrations to12 Tg N yr^{-1} and is predicted to double by 2020 (Streets and Waldhoff, 2000).

NOx emissions in Asia increased about 2.5 times from 1980 to 2000. Monitoring of air quality in Indian cities conducted by Central Pollution Control Board (CPCB) has shown a trend of dramatic increase in NOx concentrations since 1990 especially in the metropolitan cities. According to the monitoring, conducted by Garg et al. (2001), NOx emissions over the Indian region are growing at an annual rate of 5.5% year^{-1}. Annual average NOx concentrations varied from 4.3 to 42.9 ppb in various parts of the country (CPCB, 2009). In the present scenario, NO_2 concentration is critical in Howrah (eastern region) where annual mean concentration is 42.9 ppb while it was 31.8 ppb in 1990. In other parts of the country, however, NO_2 concentrations were reported within the prescribed standards (CPCB, 2009). Annual mean concentration of NO_2 ranged from 10.1 to 31.3 ppb in different zones of Varanasi city, situated in eastern Gangetic plain of U.P in 1990, whereas the same varied from 16 - 155 ppb during 1999-2001 (Trivedi et al., 2003).

Ozone (O_3)

Due to the dramatic increase in transportation sector throughout the world, atmospheric build up of secondary air pollutant O_3 has also been reported. During the past few decades, the problem of tropospheric O_3 as an air pollutant intensified several fold and assumed global concern (NRC, 2001). Ozone being a secondary pollutant is not emitted as such by any specific source, rather formed during the atmospheric photo-chemical reactions involving oxides of nitrogen and reactive hydrocarbons emitted from automobiles (Krupa and Manning, 1988). These reactions are principally controlled by sunlight and temperature as given in the reactions below:

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

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

$$O + O_2 \longrightarrow O_3$$

The increasing emissions of reactive hydrocarbons and NO_2 in the urban areas have significantly increased the ground level O_3 concentrations down wind of the emission. High levels of O_3 may be found hundred or thousand of kilometers away from the original sources, often affecting remote rural areas (Prather et al., 2003). The scale of the problem of rise in tropospheric O_3 has increased in scope during last 25 years as a result of increasing population density and transportation related activities particularly in the developing countries. Background concentration of O_3 in the troposphere has doubled in the last decade. Surface O_3 concentration has risen from an estimated pre- industrial concentration of 10 ppb to average summer concentrations between 30 and 50 ppb in the mid latitudes of the northern hemisphere with episodic levels as high as 50- 100 ppb (Morgan et al., 2006). It is predicted that surface O_3 may rise to 20% over the next 50 years due to likely three fold increases in NOx and CH_4 emissions (Prather et al., 2001).

Wang and Mauzerall (2004) predicted that daytime surface O_3 concentrations in July 2020 will exceed 55 ppb in most parts of China. The increase in annual mean O_3 concentration varied from 0.1 to 1 ppb $year^{-1}$ (Coyle et al., 2003). Permadi and Oanh (2008) reported high surface O_3 levels in Jakarta during January 2002-March 2004, which frequently exceeded the hourly national ambient air quality standard (120 ppb). A maximum 1 hr O_3 concentration was reported as 243 ppb during the dry season of 2002 was reported (Permadi and Oanh, 2008). Wang et al. (2009) analyzed the variations in the concentrations of tropospheric O_3 from 1994-2007 at a coastal site in Hong Kong, and reported an increase of 0.87 ppb/yr. In Indian region, O_3 monitoring conducted at Ahmedabad, an urban site showed O_3 concentration upto 80 ppb (Lal et al., 2000). Varshney and Aggarwal (1992) showed ground level O_3 concentrations between 9.4 - 128.3 ppb in Delhi. In another study conducted by Central Road Research Institute at seven sites in Delhi showed that 8 h O_3 concentration during day exceeded the WHO standard of 51 - 102 ppb by 10 - 40% (Singh et al., 1997).

A detailed study conducted in Varanasi, India revealed that monthly 24 h average O_3 concentration varied from 6.12-34.68 ppb from relatively clean to polluted area during 1989-1991 (Pandey and Agrawal 1992). Studies conducted during 1999 to 2000 in Varanasi city showed that 6 hours (10 AM to 4 PM) O_3 concentrations varied from 9.2 - 48 ppb in summer and 7 – 45 ppb in winters in periurban areas (Agrawal et al., 2006). Another study conducted by Agrawal et al. (2003) showed O_3 concentrations (6 h) ranging from 10.3 to 15.4 ppb during winters and from 9.7 to 58.50 ppb during summers at different sites in Varanasi city. Study conducted at suburban areas of Varanasi during 2002- 2006 reported that O_3 concentrations (12 h) ranged from 45.18- 62.35 in summer, 28.55- 44.25 ppb in winter and 24.09- 43.85 ppb in rainy season (Tiwari et al., 2008).

Concentration of NO_x and O_3 are increasing in the developing world caused by industrialization and population growth, which resulted in increase in traffic and domestic emissions (Ashmore and Marshall, 1999). Sulphur dioxide, nitrogen oxides and secondary air pollutant, O_3 are identified as major threats to crop production. These phytotoxic gases have important and increasing impacts on the livelihoods and well being of producers and consumers through effects on urban and periurban crop production. Air pollution has the potential to reduce both the yield and the nutritional quality of the crop plants (Rai et al., 2010; Ashmore and Marshall, 1999).

3. Plant responses to air pollution

Visible symptoms

Air pollutants can produce a wide range of visible symptoms (acute injury) on crops. Injury to plants as a result of pollutants has been classified as either chronic or acute. An acute SO_2 is viewed as a short duration high level of SO_2. On broad- leaved plants, acute SO_2 injury symptoms consist of bifacial, marginal and/or interveinal necrosis and chlorosis on leaves at the full stage of development. The necrotic areas can range in colour from white to reddish brown to black depending on the plant species. In monocotyledonous plants, acute injury symptoms start at the tip of the leaves and spread downward as necrotic and chlorotic streaks with occasional reddish pigmentation. Chronic SO_2 exposure may or may not result in foliar injury symptoms depending upon plant susceptibility. It is important to note that reductions in plant growth and productivity from chronic exposure may occur without development of visible chronic foliar injury (Legge and Krupa, 2002).

In case of SO_2 and NO_2, visible injury usually results from exposure to pollutant concentrations above a point around an order of magnitude greater then the threshold for growth and yield reductions in absence of visible, i.e. chronic injury, however, in case of O_3, acute visible symptoms can be produced on sensitive species within a range of approximately twice the maximum natural concentration of this pollutant. Thus, visible SO_2 and NO_2 injury is largely confined in the field to severely polluted locations or on the occasion of large industrial accidental releases. In contrast, visible O_3 injury is recorded more frequently over worldwide areas when an elevated level of this pollutant occurs. Acute injury by these pollutants vary in their form of various necrotic lesions, ranging from a fine stipple to large patches of dead tissue, with colouration ranging from white to brown black (Taylor et al., 1987).

Symptoms of NOx toxicity in plants are difficult to diagnose in the field. In angiosperm, discoloured gray green or light brown spots are formed interveinally, at times combining to form stripes, with marginal chlorosis of leaves and only the veins retain their green colouration.

The symptoms associated with O_3 injury include necrotic spots on the adaxial surface takes on a bleached appearance as these flecks coalesce. Necrosis can extend through to the abaxial side of the leaf and at high levels of O_3, water soaking can occur. Low levels of O_3 can cause chlorosis.

Uptake of Pollutants

Leaves are most susceptible parts of a plant to acute injury due to their abundance of stomata, which permit penetration of the pollutants into the sensitive tissues. The first barrier of gaseous air pollutant is boundary layer resistance which varies with wind speed and size, shape and orientation of leaves (Heath et al., 2009). At higher wind speed, boundary layer resistance declines allowing more pollutant entry into the leaf. The cells most exposed to air pollutant action are epidermal cells, but waxy cuticle is a potential barrier to most of the pollutant gases. However, acidic gases can dissociate and react with cuticular waxes and enter leaves by penetrating through damaged cuticle. Kersteins and Lendzian (1989) suggested that a reactive pollutant like O_3 might be a expected constituent, but ambient concentration of O_3 does not seem to affect the water movement through cuticle. The extent of damage that air pollutants can cause in plants depends upon the pollutant influx into the leaves and the reactivity of its reaction products with cellular constituents.

Mechanism of action

Sulphur dioxide

The response of stomata to SO_2 entry is largely dependent on leaf age, concentration and combination of pollutants (Pfanz et al., 1987). Black and Unsworth (1980) reported that low concentration of SO_2 stimulated stomatal conductance in *Vicia faba* L. within 15 mins of exposure, which persisted for several days. This has been attributed to the destruction of epidermal cells adjacent to stomata and accumulation of sulphur within guard cells. Larger stomatal apertures not only allow ingress of the damaging pollutant, but also enhance water loss due to unrestricted transpiration. Once SO_2 enters through stomata, the route to the surface of a nearby subsidiary or epidermal cell is very short and therefore, the cells of the epidermis are more susceptible. The detrimental effects of SO_2 occur due to reactions under liquid phases after their uptake in the plants. Chemical reactions and productions of reactive oxygen species (ROS) due to SO_2 absorption within the cellular space (Bartosz, 1997) are:

$HSO_3^- + {}^{\cdot}O_2^- + 2H^+ \longrightarrow HSO_3^{\cdot}$ (bisulphate radical)+ $2{}^{\cdot}OH$

$HSO_3^- + {}^{\cdot}OH + H^+ \longrightarrow HSO_3^- + H_2O$

$HSO_3^{\cdot} + O_2 \longrightarrow SO_3^{2-} + O_2^{\cdot-} + H^+$

$HSO_3^{\cdot} + {}^{\cdot}OH \longrightarrow SO_3^{2-} + H_2O$

$2HSO_3^{\cdot} \longrightarrow SO_3^{2-} + HSO_3^- + H^+$

$SO_3 + H_2O \longrightarrow SO_4^{2-} + 2H^+$

${}^{\cdot}O_2^- + {}^{\cdot}O_2^- + 2H^+ \longrightarrow O_2 + H_2O_2$

${}^{\cdot}OH + {}^{\cdot}OH \longrightarrow H_2O_2$

SO_2 readily dissolves in the apoplastic water to produce mainly sulphite (SO_3^{2}), bisulphite (HSO_3^-) and H^+ ions, reducing the pH of the medium (Legge and Krupa, 2002). The phytotoxicity of SO_2 due to SO_3^{2-} and HSO_3^- ions (DeKok, 1990). Most leaves have the capacity to detoxify, sulphite and bisulphite, if the concentrations are not excessively high, by oxidizing them to less toxic sulphate ion (Rao, 1992). Several studies have shown that the disturbances caused by SO_2 to biochemical functions (Li et al., 2007) and cell structure (Jutawong and Suwanwarer, 1997; Tripathi and Gautam, 2007) of plants appear before visual symptoms or growth reductions.

The low concentrations of SO_2 have been shown to stimulate the growth and physiological responses, especially in plants growing in sulphur deficient soil (Darrall, 1989), where SO_2 might be metabolized to fulfill the demand of sulphur as nutrient (DeKok, 1990). However, the higher uptake of SO_2 turns toxic and is reported to damage plants and reduce growth and productivity by interfering with different physiological and metabolic processes (Agrawal and Deepak, 2003; Agrawal et al., 2006).

The effects of SO_2 on physiological and biochemical characteristics of plants have been well documented (Darrall, 1989; Agrawal et al., 2006; Chauhan and Joshi, 2010). Physiological processes such as photosynthesis, respiration, stomatal activity, transpiration and translocation are reported to be adversely affected by SO_2 (Darrall, 1989; Agrawal and Deepak, 2003; Li et al., 2007). Alterations in various physiological functions were ascribed to changes in permeability of plasma membrane (Legge and Krupa, 2002), by interfering with enzymatic activities, and altering metabolic functions and nutrient uptake and water relations (Li et al., 2007). Photosynthetic pigments and many enzymes are associated with the membranes of chloroplasts. Aqueous SO_2 can cause damage to plant metabolism by acting as an electron transport system. Agrawal and Deepak (2003) studied the inhibition of photosynthetic CO_2 fixation by SO_3^- and this effect was due to competition between CO_2 and SO_3^- for active sites of ribulose 1, 5 – biphosphate carboxylase. SO_2 affects photosynthetic pigments leading to breakdown of chlorophyll (Malhotra, 1976). Studies with soybean showed significant decrease in chlorophyll content and photosynthesis rate at 60ppb SO_2 (Agrawal and Deepak, 2003). Several field experiments have shown reductions in root and shoot lengths, leaf area and number of leaves, ears, seeds and yield of plants due to SO_2 exposure (Agrawal and Deepak, 2003; Agrawal et al., 2006)

Nitrogen dioxides

The two oxides of nitrogen i.e. NO and NO_2 are toxic air pollutants, but NO is rapidly oxidizes to NO_2 in free atmosphere. The uptake of nitrogen dioxide by plants occurs predominantly by foliar deposition. The mode of entry for the majority of gaseous NO_2 is through the stomatal openings (Darrall, 1989). The entry of NO_2 into leaves is similar to that of SO_2, however, entry through cuticle is higher as cuticular resistance against NO_2 entry is lower than for SO_2 or O_3. A single exposure of *Euonymus japonica* to 100 ppb NO_2 led to an increase in stomatal conductance (Natori and Totsuka, 1984), but higher concentration may reduce the stomatal conductance (Saxe, 1986).

NO_2 after entering into the leaf, dissolves in the extracellular water of the substomatal cavity to form both HNO_2 and HNO_3, which dissociates to form nitrate, nitrite and protons as described below (Ramge et al., 1993)

$$NO_2 + H_2O \longrightarrow HNO_3$$

$$NO + H_2O \longrightarrow HNO_2$$

$$HNO_3 + HNO_2 \longrightarrow NO_3^{2-} + NO_2^{2-} + H^+$$

NO_2 and NO belongs to the rare odd electron oxides of main group elements. The ease of dimerization of nitrogen dioxide yielding di nitrogen tetraoxide shows that NO_2 is a free radical. After dissolving into the aqueous phase of the apoplast two reactions may occur: reduction by antioxidants such as ascorbic acid to produce nitrous acid (HNO_2) and dehydroascorbate (Ramage et al., 1993) or dissociation to produce nitrate (NO^{3-}) and nitrite (NO^{2-}), both powerful oxidants, may initiate hydrogen abstraction to affect the components of mesophyll and thereby initiate the production of free radicals and free radical chain reactions (Sparks et al., 2001). NO_2 is also capable of initiating peroxidation processes within lipid membrane (Ramage et al., 1993). At higher concentration, NO_2 can cause acute injuries on plant leaves, while chronic exposure to lower concentration of NO_2 reduces the growth of plants. Ultrastructural changes associated with invisible injury have often been linked to reductions in transpiration and photosynthesis.

Gaseous oxides of nitrogen often restrict the growth of plants. Relatively few studies have been reported on the effects of NO_2 on chlorophyll concentrations and growth of plants (Chen et al., 2010). Chen et al. (2010) when exposed one year old *Cinnamomum camphora* L. seedlings to 10, 50 and 400 ppb NO_2 for a period of 60 d during daytime hours (10 h/d, 7 d/week), observed increase in lipid peroxidation and reductions in above and below ground biomass, Fv/ Fm ratio, total chlorophyll, ascorbic acid content and superoxide dismutase activity at 400 ppb. In a field transect study conducted by Chauhan and Joshi (2010) in Haridwar, India to assess the effect of air pollutants on wheat and mustard crops, it was observed that site 3 receiving higher load of pollutants (SO_2 6.5 ppb and NO_2 9 ppb) showed maximum reductions in growth and yield, ascorbic acid content and photosynthetic pigments.

Ozone

Ozone is a widespread secondary photochemical air pollutant in many parts of Europe, North and Central America and Asia (Heath, 1994; Krupa, 1996). Ozone is important not only because of its phytotoxicity (Ashmore, 2005), but also because of its tropospheric concentration which has increased considerably during past 60 years (Anfossi et al., 1991) and is likely to increase at an annual rate of 0.5-2.5% for feaseable future (Coyle et al., 2003). The harmful effects of O_3 on various components of vegetation such as forest trees, agricultural crops and ornamental plants are now well recognised. When the effect is severe, death of plant organ may occur. Effects on cells and organs affect organismal growth, which ultimately leads to yield reductions (product synthesis) and quality changes. The reaction of plants to O_3 depends on the ambient levels, the amount diffusing in the leaf interior and the plants autonomous and environmentally modified resistance. The absorption of O_3 to individual plants is the consequence of the chemical potential gradient between the atmosphere and the site of deposition either on foliar surfaces or cells of the leaf interior (Mansfield and Pearson, 1996). The harmful effects of O_3 occur due to reactions under gas and liquid phases after their uptake in plants and further reactions products. The mechanism of formation of reactive oxygen species under O_3 exposure are given below:

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

$${}^{\cdot}O_2^{-} + H^{+} \longrightarrow HO^{\cdot}_2 \text{ (peroxy radical)}$$

$$.HO'_2 + {}^{\cdot}HO'_2 \longrightarrow H_2O_2 \text{ (hydrogen peroxide)} + O_2$$

$${}^{\cdot}O_2^{-} + {}^{\cdot}HO'_2 + H_2O \longrightarrow H_2O_2 + OH^{-} + O_2$$

Ozone that has passed through leaf internal air spaces dissolves in the aqueous layer. The breakdown of O_3 in pure water produces hydroxyl ($OH^{\cdot}$), peroxyl ($OH_2^{\cdot}$) and superoxide (${}^{\cdot}O_2^{-}$) radicals (Rao et al., 2000), although the reactions proceed very slowly at neutral pH (Fiscus et al., 2005). In contrast to O_3, H_2O_2 formed due to ozonolysis dissolves very well in the water phase and can be transported through the membranes and circulated within the plant. Further reactions of H_2O_2 lead to the formation of other reactive oxygen species such as superoxide and hydroxyl radicals, which can initiate lipid peroxidation, a chain reaction destroying the membranes (Loreto and Velikova, 2001). The initial site of injury caused by O_3 and /or O_3 generated ROS is the plasma membrane, resulting in changes in permeability, fluidity, potassium (K^{+}) exchange via ATPase reactions and calcium (Ca^{2+}) exclusion (Heath, 2008). A change in membrane function leading to a rise of intercellular Ca^{2+} that would lead to alteration of all sorts of intracellular metabolism (Heath, 2008).

O_3 reacts in the substomatal cavity with hydrocarbons such as ethylene and some terpenes (Sharkey and Yeh, 2001). This oxidative process (ozonolysis) also produces H_2O_2 and aldehydes in a humid environment. The internal air spaces within the leaf are a potential site for O_3 reactions and formations of toxic compound within the cellular spaces (Heath, 1994).

The plasma membranes are protected by antioxidants such as hydrophilous ascorbate (Vitamin C), lipophilous α tocopherol (Vitamin E) and enzymes such as superoxide dismutase (SOD) and peroxidases (POD). The first detoxifying barrier represents the antioxidant system found in the cell (apoplasm+ symplasm). Ascorbic acid (AA) is an integral weapon in the defence against ROS generated by O_3. Apoplastic ascorbic acid is an important first line defence against O_3 as it is maintained in a reduced state. In plant cells, the most important reducing substrate for H_2O_2 detoxification is ascorbate peroxidase, which uses two molecules of ascorbate to reduce H_2O_2 to water through a series of reactions known as the ascorbate- glutathione cycle (Noctor and Foyer, 1998). An alternative mode of H_2O_2 destruction is via peroxidases (POD), which are found throughout the cells. Ascorbic acid content increased in O_3 susceptible cultivars of snap bean with an increase in visible injury (Wu and von Tiedmann, 2002). An increase in POD activity has also been reported as a response to higher levels of H_2O_2 (Wu and von Tiedmann, 2002).

Photosynthesis (Ps), a core function in the physiology of plants is most susceptible to O_3. Reductions in Ps have been widely reported under ambient field conditions at higher concentrations of O_3 (Rai et al., 2007; Tiwari et al., 2006, Calatayud et al., 2002; Agrawal et al., 2003). Meta analytical analyses on several varieties of wheat (Feng et al., 2008), soybean (Morgan et al., 2003, 2006) and rice (Ainsworth, 2008) also found varying degrees of response of photosynthesis to O_3. O_3 caused reduction in level of RNA transcript for the small subunit (rbcS) of Rubisco and also decreased the expression of photosynthetic genes including Rubisco and Rubisco activase. O_3 leads to reductions in m RNA levels of both small (rbcS) and large (rbcL) subunits of Rubisco of wheat cultivars M 510 and Sonalika (Sarkar et al., 2010) grown in open top chambers (OTCs) receiving ambient+ 10 ppb and ambient+ 20 ppb O_3. In a proteomic analysis conducted in- vivo condition on rice seedlings exposed to O_3 (40, 80, 120 ppb for 6 h d^{-1} for 9 d), reduction in expression of Rubisco large subunit (LSU) and small subunit (SSU) was reported (Feng et al., 2008).

Reductions in photosynthesis affect carbon assimilation, translocation and accumulation in different plant parts. Ozone leads to inhibitory effects on phloem loading. The exposure of foliage to O_3 resulted in an accumulation of carbohydrate in the source leaves and reduced translocation to distant sink

(Grantz and Yang, 2000). The pattern of photosynthate allocation directly affects the plant growth and reproduction. O_3 exposure reduced the available carbohydrates to roots in soybean (Morgan et al., 2003), wheat (Biswas et al., 2007), cotton (Grantz and Yang, 2000) and a number of other crops (Cooley and Manning, 1987; Andersen, 2003). Even, the changes in the supply of or competition for assimilates, or in the synthesis and distribution of hormones required for the successful seed development and maturation, may affect the yield in grain crops. Studies have shown that O_3 exposure reduced yield in grain crops by decreasing ear and pod numbers (Black et al., 2007). Grain yield in cereals is reduced by the effect of air pollutants on rate and the duration of grain filling due to impairment of production in carbohydrates and translocation of assimilates from the source organs to the grains (Gelang et al., 2000).

Exposure to air pollutants may also induce negative impact on reproductive processes. These include modulation of pollen or ovule maturation; changes in the timing, rate or number of flowers produced, effects on seed and fruit development, yield, seeds germinability and seedling vigour (Black et al., 2000).

The impact of O_3 is known to vary between species and cultivars (Black et al., 2007; Biswas et al., 2007; Rai et al., 2010) and to be influenced by both climatic factors (Emberson et al., 2000; Health et al 2009) and cultural practices (Singh et al., 2009). There is abundant evidence that current ambient O_3 concentration in many industrialized areas of the world are sufficient to cause significant yield losses in both agricultural and native species (Heagle et al., 1988; Rai et al., 2007, Shi et al., 2009; Sarkar and Agrawal, 2010) .

4. Economic assessment of crop loss due to air pollution

Crop production is highly dependent upon environmental conditions among which air quality plays a central role. The studies conducted in North America and Europe have clearly shown significant yield losses in a range of major crop species due to ambient air pollutant levels prevailing in the rural areas (Heck et al., 1988). Heck et al. (1982) estimated the annual loss of $1.0 to $ 2.0 billion due to air pollution of which O_3 either alone or in combination with SO_2 or NO_2 accounted for 90% of the damage in U.S.A. Lee (1999) estimated the air pollution led losses of $ 4.0 to 5.0 billion in U.S.A. due to reduction in major crop yields. Wahid et al. (1995) have demonstrated grain yield reductions of 46 and 38% for two cultivars of winter wheat through open top chamber studies conducted in the vicinity of Lahore, Pakistan using ambient and charcoal filtered air. Maggs et al. (1995) have further shown significant reductions in various yield parameters of both wheat and rice at annual mean NO_2 concentration of 20-25 ppb and 6 h mean O_3 concentration reaching 60 ppb in certain months. Wahid (2006) reported reductions of 43, 39 and 18% in yield of three wheat cultivars Pasban 90, Punjab 96, Inquilab 91, respectively at seasonal mean concentrations of 70, 28 and 15 ppb O_3, NO_2 and SO_2, respectively at Lahore, Pakistan.

In an open top chamber study conducted at suburban site in Varanasi, Rai et al. (2007) reported 20.7% reduction in yield of wheat cultivar M 234 grown at ambient air pollution level (SO_2 7.8 ppb, NO_2 40.6 ppb, O_3 42.1 ppb) and at rural site in Varanasi, experiencing low concentrations of SO_2 7.3 ppb and NO_2 14.5 ppb and high O_3 concentration (35 ppb) found 10 and 14% reduction in yield of rice cultivars NDR 97 and Saurabh 950 grown at ambient air (Rai and Agrawal, 2008).

Adams et al. (1984) have compared three O_3 scenarios with a base case of 1978 in USA and estimated that the total welfare gain from a reduction in ambient O_3 by approximately 25% (seasonal 7 hrs mean 40 ppb) was $ 35.8 million annum^{-1} and welfare loss from an increase in O_3 levels by approximately 33% (i.e. 80 ppb seasonal 7 hr mean) was $ 157.3 million per annum. Data generated from National Crop Loss Assessment Network (NCLAN) exposure crop response regression analyses indicated that at least 50% of the species / cultivars tested were predicted to exhibit 10% yield loss at 7 h seasonal O_3 concentrations of < 50 ppb (USEPA, 1996). Estimation of yield losses due to O_3 exposures accounted for 2 - 4% of total US crop production (Adams et al., 1988). Reducing VOCs/NO_x from motor vehicle emissions by 10% would result in a benefit of US $ 0.3 billion, while a complete elimination of motor vehicle emissions would yield a benefit of US $3.4 billion (Murphy et al., 1999).

Murphy et al. (1999) evaluated the benefits to eight major crops associated with several scenarios concerning the reduction or elimination of O_3 precursor emissions from motor vehicles in the United States. Their analysis reported a benefits from US $2.8 to 5.8 billion due to complete elimination of O_3 exposures from all sources, i.e., ambient O_3 reduced to a background level assumed to be 25 to 27 ppb. The other studies in U.S.A. projecting economic loss of yield for all crops under O_3 pollution depict amounts of US $ 3 billion by Heck et al. (1988), US $ 0.1 – 2.5 billion by Adams and Horst (2003) and US $ 3 – 5 billion by Fiscus et al. (2005) and USEPA (2006).

Kuik et al. (2000) reported economic loss of 310 million euros in all crops of the Netherlands under ambient O_3. Evaluation of the economic impact of O_3 on crop yield has indicated a loss of 4 billion Euros in Europe for all crops in the country (Holland et al., 2002) and 0.049 billion Euros for 23 horticultural and agricultural crops (Holland et al., 2006). Wang and Mauzerall (2004) translated the current day yield loss estimates into economic losses of approximately US $ 5 billion for wheat, rice, maize and soybean grown in China, Japan and South Korea. Using a global chemistry transport model a global economic loss in the range of US $ 14 – 26 billion has been calculated at world market prices for the year 2000 by Van Diengenen (2009). In India, there are limited reports on economic loss for different crops due to air pollution, studies showed economic loss were in the range of Rs 30,550- 1, 208 ha^{-1} for major agricultural crops wheat, rice, mustard, urd, soybean, pea and mung (Table 2). These economic losses were calculated using different study approaches such as field transect study, open top chambers and ethylene diurea (EDU) based studies on different cultivars of wheat, rice, mustard, urd, soybean, pea and mung.

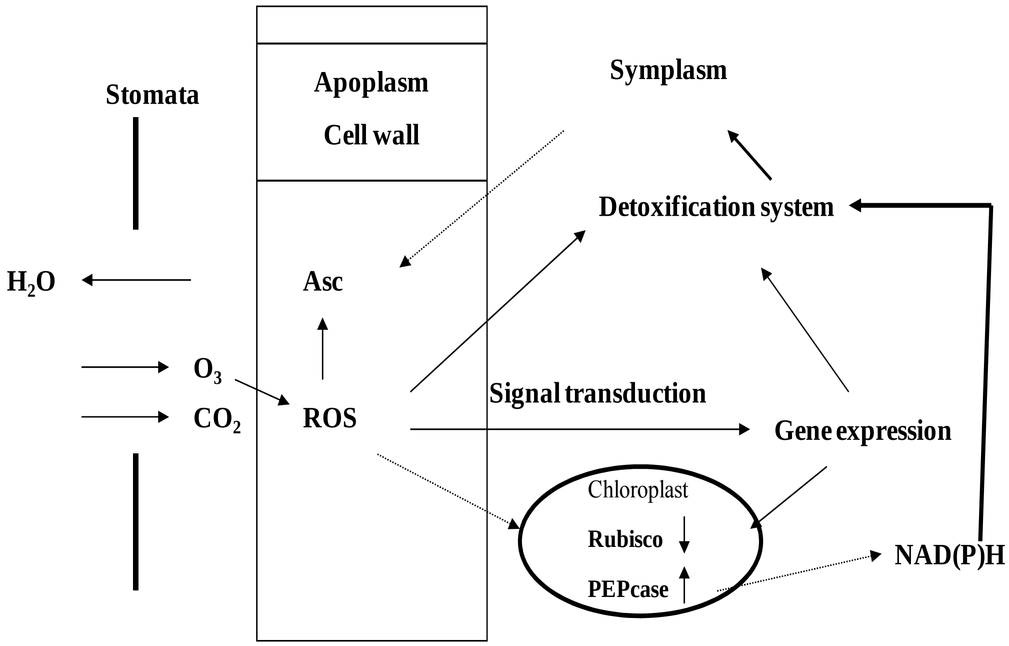

Figure 1 : Summary of the relationships between stomatal uptake, metabolic changes and detoxification system under chronic ozone attack in plant cells. Asc= ascorbate, PEPcase= phosphoenolpyruvate carboxylase, ROS= reactive oxygen species, Rubisco= ribulose-1,5-bisphosphate carboxylase (Source: Dizengremel et al., 2008)

Table 1 : National ambient air quality standards given by CPCB (November, 2009)

Pollutant	Time weighted Average	Concentration in ambient air			
		Industrial, residential, rural and other area		Ecologically sensitive area	
		(μg m^{-3})	(ppb)	(μg m^{-3})	(ppb)
Sulphur di oxide (SO_2)	Annual*	50	19	20	8
	24 hours**	80	30.4	80	30.4
Nitrogen di oxide (NO_2)	Annual*	40	21.2	30	15.9
	24 hours**	80	42.4	80	42.4
Ozone (O_3)	Annual*	100	51	100	51
	1 hour**	180	91.8	180	91.8

* Annual arithmetic mean of minimum 104 measurement taken in a year at a particular site twice a week, 24 hourly at uniform levels.

** 24 hourly or 1 hourly monitored values as applicable shall be complied with 98% of the time, 2% of the time, they may exceed the limits but not on two consecutive days of monitoring.

Table 2 : Estimates of economic loss for different crops due to air pollution in India

Crops/Cultivars	Economic loss (Rs ha^{-1})	Pollutant regime (ppb)			Studies approach
		SO_2	NO_2	O_3	
Wheat					
M 234	23846	8	40	42	OTCs
PBW 343	1620	11	20	45	OTCs
M 533	1641	11	20	45	OTCs
M 510	14040	-	-	47	OTCs
Sonalika	5389	-	-	47	OTCs
Lok-1	5055	6.1	13	48	OTCs
HD2329	12505- 17995	18-45	28- 47	10- 15	FTS
M234	4156	-	-	44	EDU
M 468	11016	-	-	44	EDU
M 510	8964	-	-	44	EDU
PBW 343	1080	-	-	44	EDU
Sonalika	5724	-	-	44	EDU
HD 2329	13176	8.5	13.5	29	EDU
Rice					
NDR 97	4246	7.3	14.5	35	OTCs
Saurabh 950	1972	7.3	14.5	35	OTCs
Mustard					
Kranti	7481	6.1	13	48	OTCs
Aashirwad	8445	6.1	13	48	OTCs
Vardan	3587	6.1	13	48	OTCs
Pusa Jaikisan	1208- 5453	18-45	28- 47	10- 15	FTS
Urd					
Barkha	3096	-	-	51	EDU
Shekhar	1135	-	-	51	EDU
Soybean					
Pusa 9712	9907	-	-	52	EDU
Pusa 9814	7776	-	-	52	EDU
Pea					
Arkel	19012- 30550	18-45	28- 47	10- 15	FTS
Mung					
Malviya Jagriti	7860-13244	13- 32	12- 80	10- 58	FTS
Malviya Janpriya	5972	9	17.5	59	EDU

Minimum support price (2009) : Rs 18.3 kg^{-1} for mustard, Rs 10.8 kg^{-1} for wheat, Rs 5.7 kg^{-1} for rice, Rs 17.2 kg^{-1} for urd, Rs 13.5 kg^{-1} for soybean, Rs 25.2 kg^{-1} for mung OTCs : Open Top Chamber; FTS : Field transect study; EDU: Ethylene diurea.

5. Conclusions

The collated information based on field experiments concludes that air pollutants not only affect the vegetation near the point sources and urban centres, but depending on the meteorology, specially wind pattern may spread in suburban and rural areas, affecting the crops. Air pollutants cause deleterious effects on physiology and metabolism of plants due to their oxidizing potential. Responses of plants vary between different species and their cultivars. Responses of plants to air pollutants also depend on type of pollutants, concentrations duration and its magnitude. There is a need to screen out sensitive and tolerant cultivars in India and establish the exposure indices of all the important crops to reduce the crop loss.

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