INTRODUCTION
The air, water, soil, plants and animals constitute the natural capital on which man depends to satisfy his needs and achieve the desired development. Wise management of these resources demands a positive and realistic planning that balances human needs against the potential the environment possesses for meeting them. This is why the decision makers, scientists, social workers and even laymen are becoming increasingly conscious of a variety of environmental issues.

Pollution, whether of air, water or land, is a man-made problem with far-reaching repercussions. Most industries release toxic metals or untreated effluents which go to rivers, and via the water systems and plant kingdom are passed on to man. Gaseous air pollutants affect plants mainly by two ways. They are either dissolved in rain or fog droplets and reach the plant surface in the aqueous from or diffuse into the interior of the tree organs in their dry gaseous form. In the first case, the dissolved pollutants accumulate at the surface of plant parts but do not reach easily the more protected tissues in the interior of the organs. In the second case, the gaseous molecules (e.g., $\text{SO}_2$, $\text{NO}_x$, $\text{CO}_2$ or HF) permeate into the intercellular air spaces by pore diffusion via the stomates and/or lenticels (Pfanz et al., 1998).

Concentrations of many atmospheric trace gases have been increasing since the onset of industrial revolution, thus overloading the whole system with atmospheric pollution. Some such gases, when present in high concentration and frequency, have adverse effects on plants and ecosystem (Guderian, 1985; Legge et al., 1986; Krupa
et al., 1994). In major metropolitan cities of India, air pollution has become a serious problem as a result of the fast-expanding industrialization and urbanization (Sivacoumar et al., 2001). India has as many as 75 thermal power plants, releasing enormous amounts of sulfur dioxide, nitrogen oxides, carbon monoxide, hydrocarbons, fluorine, flyash and other particulates (Iqbal et al., 2000b) (Table 1).

The coal-fired power plants release pollutants in the atmosphere on combustion of coal (Hesketh, 1973). On complete burning of the fuel the combustion products in the air, contain sulphur dioxide, nitrogen oxide, carbon dioxide, water, sulfite oxide and ash. With an incomplete combustion, pollutants like carbon monoxide, hydrocarbons, \( \text{CH}_4 \), \( \text{C}_2\text{H}_4 \) and some carcinogenic substances may also form additionally. These power-plants are the major contributors of deadly fine particles (soot), asthma inducing smog, toxic emissions of mercury, acid rain forming oxides, and carbon dioxide emissions which cause global warming. Flyash, the most hazardous inorganic product of coal combustion in the boilers of thermal power plants, is thrown up as a fine powder waste material (Rathor et al., 1985).

Garg et al. (2001) have reported emission estimates from 94 power plants (81 coal, 12 gas and one oil based), 11 steel plants, 92 cement plants, 31 fertilizer plants, 12 petroleum refineries and 26 other sources including petrochemicals and smelting units which deteriorate the environmental conditions.

Total \( \text{SO}_2 \) emissions in India were estimated at 3.54 Tg in 1990 and 4.64 Tg in 1995. In 1990, 64% of total \( \text{SO}_2 \) emissions emanated from coal consumption, 29% from oil products, 4.5% from biomass and 2.5% from non-energy consumption. Emissions from natural gas were insignificant. Interestingly, composition of emissions from different fuels remained similar in 1990 and 1995 with a marginal increase in
<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Pollutant Gas</th>
<th>Sources</th>
<th>Plant injury symptoms on leaves</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sulfur dioxide (SO$_2$)</td>
<td>Coal, fuel oil, and petroleum combustion</td>
<td>Interveinal chlorosis, necrosis, bronzing; red brown dieback and banding</td>
</tr>
<tr>
<td>2</td>
<td>Nitrogen oxides (NO$_x$)</td>
<td>High-temperature combustion of fuels in power plants; internal combustion engine</td>
<td>Interveinal bronzing as by SO$_2$; red-brown distal necrosis</td>
</tr>
<tr>
<td>3</td>
<td>Suspended Particulates (SPM)</td>
<td>Incomplete combustion; fly ash; cement factories; metal smelters; auto exhausts</td>
<td>Surface deposition, serious effects according to chemical nature of dust</td>
</tr>
<tr>
<td>4</td>
<td>Ozone (O$_3$)</td>
<td>Atmospheric reactions in urban and industrial areas</td>
<td>Upper-surface flecks, needle point chlorotic dots, chlorosis, necrosis</td>
</tr>
<tr>
<td>5</td>
<td>Peroxy-acetyl nitrate (PAN)</td>
<td>Atmospheric reactions in industrial areas</td>
<td>Lower surface bronzing, chlorosis, early senescence</td>
</tr>
<tr>
<td>6</td>
<td>Smog</td>
<td>Atmospheric reactions in industrial areas</td>
<td>Chlorosis banding on grass blades, chlorosis, necrosis as with O$_3$</td>
</tr>
</tbody>
</table>
the share of emissions from coal and a corresponding reduction in emission from biomass. Two thirds of the increase in SO\textsubscript{2} emissions during 1990-1995 were due to consumption of coal. The increase in coal-based SO\textsubscript{2} was because of an increased electric power generation (Garg et al., 2001).

Sector-specific emissions indicated a dominance of electric power generation sector, contributing 46% of the all India SO\textsubscript{2} emissions in 1995 (Fig.1). Industry was the second largest SO\textsubscript{2} emitter at 36%, followed by transport (7.8%), biomass consumption (6%) and other sectors (3.8%) (Fig.2). India’s power sector is mainly growing on coal with its total coal and lignite consumption increasing heavily, e.g. by above 60% between 1990 and 1995. However, since the Indian coal has a lower sulfur content, the impact of increased coal usage has not been so pronounced in absolute terms. Indian power sector continued to be dominated by sub-critical pulverized coal technology with about 7.0 tons SO\textsubscript{2} emissions per GWh during 1990-1995 (Garg et al., 2001).

The regional spread of overall SO\textsubscript{2} emissions per unit area varies widely across the Indian districts and has a close correspondence with coal-consumption pattern. The emissions from a province also indicate a good correlation with its population and level of economic activity. Higher population implies higher level of economic activities and correspondingly higher-energy consumption as the energy elasticity of the Indian GDP has been above unity for the last 20 yr (ESI, 1999; CMIE, 1999). Uttar Pradesh happens to be the most populous province of the country and heads the list of SO\textsubscript{2} emissions as well. Net State Domestic Product (NSDP) captures the level of economic activity of a province and the eight provinces with highest NSDP (CMIE, 1994, 1997) are also the top SO\textsubscript{2} emitters in the country. The
Fig. 1: Sectoral shares of SO₂ emissions.

Fig. 2: Details of Industrial SO₂ emissions.

Fig. 3: Sectoral shares of NO₂ emissions.
national average per capita SO$_2$ emission was 4.2 kg per person in 1990, which rose to 5 kg in 1995, an increase of almost 20% in 5 years.

India emitted 3.46 Tg NO$_x$ in 1995, as per the estimates of Garg et al. (2001), and these grew at about 5.6% per annum between 1990 and 1995. Coal and oil product combustion have almost equal shares in total NO$_x$ in total NO$_x$ emissions growing around 7.2% per annum. The shares were 36% in 1990 and marginally increased in 1995 (41% for coal and 38% for oil products).

The sectoral composition indicates that transport sector has been the predominant source of NO$_x$ emissions in India contributing 32%, out of which road transport contributed around (28%), Electric power generation (28%), industry (19%), biomass consumption (19%) and other industries (2%) (Fig.3). All India NO$_x$ emissions rose by one-third between 1990 and 1995 at a CAGR of 5.6%, however sectoral emissions had wide variations. These increased by 63%, 46%, 19% and 10% for electric power generation, transport, industry and other sectors, respectively. The regional distribution also indicated a close relationship with coal as well as oil products consumption. Districts with big thermal power plants and large vehicular population emitted more NO$_x$ (Garg et al., 2001).

Properties of flyash are dependent on the composition of parent coal, conditions during combustion, efficiency of emission control devices, and the storage and handling of other byproducts. Fly ash consists of dehydrated and dissociated clay mineral impurities along with a small amount of unburnt coal, the major constituents being SiO$_2$, Al$_2$O$_3$, FeO$_3$, CaO, CaSO$_4$ and some trace elements such as Mo, Hg, Se and Cd which may be highly toxic.
In India, production of flyash from different thermal power plants has exceeded 100 million tonnes per year. The varying levels of flyash affect pH, electrical conductivity (EC) and the elemental budget of the soil. Soil pH may decrease while EC increase with the increasing amounts of flyash (Khan et al., 1996). The enhanced plant growth, as sometimes observed with a low concentration of flyash, may be attributed to an increased availability of elements essential for plant growth. Cu, Zn, Mn, and Fe, constitute a component of several enzymes involved in the carbohydrate and cell wall metabolism but become toxic in high concentrations.

Coal dust particles depending on their size and weight, may remain in the air for varying lengths of time, causing problems for agro-ecosystem in the vicinity of the coal-fired areas (Pandey et al., 1991).

In the major metropolitan cities of India, vehicular, exhaust accounts for over 70% of the total pollutant, 10-50% of the total hydrocarbons, 30-40% of the total oxides and 30% of the total particulate matter (Agrawal and Agrawal, 1989). It is estimated that in major metropolitan Indian cities about 800 to 1000 tonnes of pollutants are ejected into the atmosphere everyday (Rangarajan et al., 1995).

The industrial areas of Delhi, one of the important centres for commerce, trade and industries in northern India, are predominated by engineering, textile, foundry, glass-ceramics and chemical industries. The number of air polluting industries here is said to have exceeded 10,000. The major industries include four thermal power stations and one each of chemical, pesticides and cement-grinding units. There three coal-based and one gas-based thermal power plants located in Delhi metropolitan area are: (a) Badarpur Thermal Power Station (BTPS), (b) Indraprastha Thermal Power Station (ITPS), (c) Rajghat Thermal Power Station (RTPS) and (d)
Gas Turbine Power Station. BTPS produces 63%, ITPS 25% and RTPS 12% of the total air pollution due to thermal power plants in Delhi (CPCB, 1993-1994) (Table 2).

Delhi was among the top five $SO_2$ emitters for 1990 due to its high transport sector $SO_2$ emissions (Garg et al., 2001). Most of the $SO_2$ emissions in Delhi comes from industrial sources and power stations. The total anthropogenic $SO_2$ emission is approximately 59000 tonnes per annum (NEERI, 1991a).

Pollution stress in a forest ecosystem is superimposed upon and interacts with the naturally occurring biotic and abiotic stresses, and may accelerate the processes of changes already underway within ecosystems (Alscher and Wellburn, 1994). The stress due to regionally transported deposition and gaseous pollutants can cause structural and functional changes in plant communities (Kozlowski, 1985).

Air pollutants may affect development of plants and growth directly by altering the biochemical and physiological processes. The biochemical changes induced in cells sequentially lead to changes in metabolic pathways of the whole organism. Loss of integrity of cytoplasmic membranes affects diffusion of water and solutes and thereby the breakdown of cellular components that eventually are expressed in the form of chlorosis, necrosis, senescence of leaves and other organs, and often death of trees. Air pollutants also induce changes that do not produce visible injury symptoms but adversely affect growth, yield and quality of plants and plant products (Kozlowski, 1990).

Plant growth is influenced by air pollution in and around the urban-industrial areas. Some higher plants are very sensitive to air pollutants and show more or less specific visible and measurable effects in morphology, physiology, biochemistry and
<table>
<thead>
<tr>
<th>S.No</th>
<th>Thermal Power</th>
<th>Location</th>
<th>Capacity</th>
<th>Units</th>
<th>Fuel</th>
<th>Emission control device</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Badarpur Thermal Power Station (BTPS) Badarpur, (National Thermal Power Corporation)</td>
<td>South-East near Delhi Haryana border</td>
<td>720 MW</td>
<td>3 x 100 MW 2 x 210 MW</td>
<td>Coal</td>
<td>Electrostatic Precipitators (ESP’s) for Particulate Emissions</td>
</tr>
<tr>
<td>2.</td>
<td>Indraprastha Thermal Power Station (ITPS) (Delhi Electric Supply Undertaking)</td>
<td>Central Delhi western bank of river Yamuna of main ring road</td>
<td>283.5 MW</td>
<td>3 x 62.5 MW 1 x 60 MW 1 x 36 MW</td>
<td>Coal</td>
<td>Electrostatic Precipitators (ESP’s) for Particulate Emissions</td>
</tr>
<tr>
<td>3.</td>
<td>Rajghat Thermal Power Station (RTPS), (Delhi Electric Supply Undertaking)</td>
<td>Central Delhi near Rajghat</td>
<td>135 MW</td>
<td>2 x 67.5 MW</td>
<td>Coal</td>
<td>Electrostatic Precipitators (ESP’s) for Particulate Emissions</td>
</tr>
<tr>
<td>4.</td>
<td>Gas Turbine Power Station (Delhi Electric Supply Undertaking)</td>
<td>Central Delhi western bank of river Yamuna of main ring road</td>
<td>180 MW</td>
<td>3 x 60 MW</td>
<td>CNG/Naptha</td>
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the overall process of growth (Agrawal, 1985). That the quality of plant products deteriorates around thermal power plants in India is well established. Plants growing under field conditions near thermal power plants are exposed to an array of air pollutants which interact and affect plant morphology and metabolism. These effects may be synergistic, additive or antagonistic, depending on the local environmental factors and the species involved (Tingey and Reinert, 1975).

Air pollutants may also influence wood structure (Pozgaj et al., 1996). However, trees could not receive enough attention and virtually information is to meagre on the impact of environmental degradation on radial growth of woody plants. Trees have to be exposed to air pollutants constantly for long periods; they absorb and accumulate pollutants from the environment, often inflicting great damage on internal processes (Jabeen and Abraham, 1998).

Air pollutants such as SO$_2$, HF, NO$_x$ influence plant physiology on their own or in association with certain climatic factors (e.g. drought). SO$_2$ affects needles/leaves of trees and, therefore, hinders with assimilation process (Maas, 1987, Rennenberg and Herschbach, 1996). The coniferous trees are especially sensitive to such conditions. Trees are considered as active bioindicators of air pollution (Eckstein et al., 1981; Braun and Lewark, 1986) as they sensitively react to all interferences. The interference may cause severe reduction in carbohydrates in the roots and disturb cell differentiation of the secondary xylem. Exposure to SO$_2$ hampers CO$_2$ uptake in most plant species. The reduced activity of photosynthesis, in turn, may retard cambial activity and consequently the wood production which could be markedly hampered even in the absence of any visible injury. The spruce and fir trees react to air pollution, showing a decrease in sapwood width leading to a reduced water
transport in young xylem of the stem. This must reduce tree vitality. Density of wood can be a good quantitative pointer of cambial activity, thus indicating the influence of air pollution on radial growth. Trees with different sensitivity to pollution differ in wood anatomy, and fumigation has an impact on wood quality, particularly on wood density, depending on the sensitivity of trees. Wood anatomy reflects recovery process in trees after the cessation of pollution (Eckstein et al., 1995).

Although the individual results are controversial, it is agreed that wood quality is affected by industrial emissions (Halbwachs and Kisser, 1967; Grill et al., 1979; Halbwachs and Wimmer, 1987; Kartusch, 1988; Wimmer, 1993). Most changes in wood structure and quality do not, however, result in overall changes in wood properties.

In the affected areas, there has been a drastic reduction in the number of tree families represented in the forest flora. *Cecropia* is an example of a pollution-tolerant genus of which a large number of trees can be seen in the polluted areas (Segala Alves, 1995). Further changes brought about by air pollutants include a decrease in the annual-ring width, and the ring width/density ratio.

The cambial activity depends on several parameters such as water, soluble sugar and starch contents. The atmospheric pollutants inhibit photosynthesis and thus, decrease the amount of carbohydrates which are needed for normal cambial activity.

The use of woody perennials in the production of biomass as a replacement for the fossil fuel-derived energy has been suggested for reducing the rate of increases in atmospheric CO₂ (Vitousek, 1991). It is important that the ways in which trees and wood products are utilized to provide a carbon store must be assessed effectively and rapidly (Jones, 1992).
The present study was aimed at studying (a) the effects of emissions of a thermal power plant on the structural and functional properties of the leaves of *Dalbergia sissoo* Roxb. ex DC. and then (b) the influence of alteration in these parameters on cambial activity and wood production.

**MAJOR AIR POLLUTANTS AND THEIR ACTION MECHANISMS**

(a) **Oxides of Sulphur**

The most important oxide of sulphur emitted by pollution sources is sulphur dioxide (SO$_2$). It is a colourless gas with a characteristic, intense acrid odour sparingly soluble in water, yielding a weakly acidic solution of sulphurous acid, (H$_2$SO$_3$). In clean air, SO$_2$ reacts with other natural components or pollutants present in the atmosphere to form sulphur trioxide, sulphuric acid and salts of sulphuric acid. Sulphur trioxide (SO$_3$) is generally emitted along with SO$_2$ at about 1-5% of SO$_2$ concentration. SO$_3$ rapidly combines with moisture in the atmosphere to form sulphuric acid. Both SO$_2$ and SO$_3$ are washed out of the atmosphere by rain or as aerosols. This is the main cause of low SO$_2$ mass in clean dry air despite heavy annual emission from anthropogenic sources.

The major source of sulphur dioxide is the combustion of fossil fuels containing sulphur. These are coal and fuel oil (natural gas, petrol diesel fuels have a relatively low sulphur content). Nearly 67% of the oxides of sulphur pollution is from volcanoes and other natural processes. The burning of fossil fuels accounts for 74% emissions and other industries for 22%. The widespread use of coal and fossil fuels for generation of electric power and other energy sources has been responsible for emission of large quantities of sulphur dioxide. SO$_2$ is largely emitted by high
stack power plants, acid sulphates can be transported over large distances (Spengler, et al., 1990).

Many factors, including temperature, humidity, light intensity, atmospheric transport and surface characteristics of particulate matter, may influence the atmospheric chemical reactions of sulphur dioxide. SO\textsubscript{2} and other pollutants, emitted at high level may be transported over very large distances by the atmosphere. During such transport processes, oxidation of sulphur and nitrogen oxides to sulphuric and nitric acids takes place giving rise to an 'acid rain' problem at downwind distances.

SO\textsubscript{2} is highly soluble in aqueous phases, but can also penetrate biomembranes (Fanz et al., 1987). It may absorb moisture from the air to form sulphuric acid mist or may react with other compounds to form sulphate. It readily goes into solution with water to form H\textsubscript{2}SO\textsubscript{3} (Singh and Rao, 1979).

The oxidation processes of SO\textsubscript{2} in gas-phase and aqueous phase involve atmospheric oxygen, ozone, hydroxyl and/or hydrogen peroxide radicals (oxidants). In gas-phase the oxidation generally occurs by reaction with hydroxyl radicals and in the aqueous-phase the major oxidants are H\textsubscript{2}O\textsubscript{2}, O\textsubscript{3} or O\textsubscript{2} (catalyzed by iron and manganese) depending on concentrations and pH. H\textsubscript{2}O\textsubscript{2} is probably the dominant aqueous-phase oxidant because of its high solubility and rapid reactivity (Brueggemann and Spindler, 1999).

SO\textsubscript{2} concentrations in the industrial areas are several times higher than the normal levels. The concentrations may be highest in winter and autumn, because of the higher SO\textsubscript{2} emissions from the still dominating use of lignite as a source of fuel and due to the lower chemical transformation rates in the colder and darker months (Brueggemann and Spindler, 1999).
Sulphur compounds in solution are chemically reactive both as oxidizing as well as reducing agents, and hence many forms of material damage can be ascribed to the atmospheric levels of sulphur compounds. Sulphur dioxide may be a reducing or oxidizing agent depending upon the pH of the medium in which it exists. In general, an acidic solution favours the formation of $\text{H}_2\text{SO}_3$ and $\text{HSO}_3^-$, while an alkaline solution favours the formation of $\text{SO}_3^2-$. It may also be oxidized to $\text{SO}_4^{2-}$. Approximately 50% of $\text{SO}_2$ occurs in the form of $\text{HSO}_3^-$ and 50% in the form of $\text{SO}_3^-$. (Cotton and Wilkinson, 1966).

In solution, $\text{SO}_2$ establishes the following equilibria which have an important bearing on its effects.

\[
\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3
\]

\[
\text{H}_2\text{SO}_3 \rightleftharpoons \text{H}^+ + \text{HSO}_3^-, \text{pK} = 1.76
\]

\[
\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^-, \text{pK} = 7.20
\]

Acidity can be determined by measuring the strong acids ($\text{H}^+$), $\text{H}_2\text{SO}_4$, and $\text{HNO}_3$. Sulphate measurements were also used as surrogates for aerosol acidity, but the two measurements were sometimes weakly correlated (Monn, 2001).

$\text{SO}_2$ is a major phytotoxic component of coal-smoke which may cause serious short-term and long-term effects on vegetation. Acute exposure to high levels of the gas kills leaf tissue (leaf necrosis). The edges of leaves and the areas between the leaf veins are particularly damaged. Chronic exposure of plants to sulphur dioxide causes chlorosis, a bleaching or yellowing of the normally green portions of the leaf. Plant injury increases with increasing relative humidity. Plants incur most injury from sulphur dioxide when their stomata are open. Sulphur dioxide in the atmosphere is converted to sulphuric acid, so that in areas with high levels of sulphur dioxide
pollution. Plants may be damaged by sulphuric acid aerosols. Such damage appears as small spots where sulphuric acid droplets have impinged on leaves.

SO₂ can interact with leaves of a plant through (a) dry deposition on the cuticle, (b) wet deposition on the cuticle, and (c) diffusion through stomata, the last being the major mode of SO₂ absorption. Because of its high solubility in water, large amounts of SO₂ are absorbed to external plant surfaces when they are wet. In the dry condition, sulphur dioxide is readily absorbed by tree leaves and rapidly oxidized to sulphate in the mesophyll cells. At low uptake rates, sulphur dioxide is presumed to be oxidized almost as rapidly as it is absorbed (Bennett and Hill, 1975).

After entering the stomatal chamber, SO₂ dissolves inside the leaves in the aqueous phase of cell walls (apoplastic space) and may then diffuse across the biomembrane barrier of the plasmalemma into the cytosol of leaf cells (Takahama et al., 1992). The oxidative detoxification of SO₂ in the apoplast outside the cells is slow. Its rate depends on the rate of apoplastic hydrogen peroxide generation and on the steady-state apoplastic concentrations of phenolics and sulfite. The affinity of peroxidase for phenolics is higher than that for sulfite (Takahama et al., 1992). SO₂ deposited on moist leaf surfaces, or in contact with water precipitated onto dry leaf surfaces, will solubilize according to the reaction $\text{SO}_2^{\text{(gas)}} \leftrightarrow \text{SO}_2^{\text{(aqueous)}}$ (Cape, 1984).

$\text{SO}_2$ concentrations in the gas phase inside the leaf are low because $\text{SO}_2$ rapidly dissolves in the aqueous phase of the cell wall and reacts with water to form sulphite ($\text{SO}_2^2$), bisulphite ($\text{HSO}_3$) and other species, which ultimately will be oxidized to sulphate (Babich and Stotzky, 1980; Johnson and Jacobs, 1983; Pfaz and Dietz, 1987; Pfanz et al., 1998).
At low SO$_2$ concentrations plants can oxidize SO$_2$ into sulphite or sulphate more efficiently than at higher concentrations when their metabolic system gets much affected and the oxidation process is either very slow or completely stopped. The higher sulphate accumulation in plants exposed to a low SO$_2^-$ concentration for a long time, gives evidence to this effect (Singh and Rao, 1980). With low rate of entry, sulphur can enter the normal, metabolic pathways without any visible injury. However, if sulphur enters in excess of plant requirement, chronic injury characterized by general chlorosis (Yellowing) develops (Malhotra and Hocking, 1976).

The phytotoxic effects of SO$_2$ are greatly influenced by the ability of plant tissue to convert the dissolved SO$_2$ into relatively less toxic forms. Plants can overcome the phytotoxic effects of SO$_3^{2-}$ and HSO$_3^-$ by converting them to the less toxic SO$_4^{2-}$ (Puckett et al., 1973). Sulphate ions are produced by a free radical chain reaction and assimilated. At high levels of exposure, SO$_2$ gas and S anion (HSO$_3^-$ and SO$_3^{2-}$) can accumulate and uncouple photophosphorylation (Silvius et al., 1975).

Sulphate can be metabolized by most of the plants. The concentration of the intermediate oxidation products of SO$_2$ in leaves attains steady values depending on the rate of entry of SO$_2$ and on rates of metabolism and translocation. The increasing trend in the SO$_4^{2-}$ levels from the non-injured to injured leaves at polluted site could be due to the increasing accumulation of SO$_3^-$. This was supported by a parallel, declining trend in the organic (metabolized) S content from the non-injured to injured leaves as observed in Saskatoon serviceberry (*Amelanchier alnifolia* Nutt.) cv. Smokey (Krupa and Legge, 2001).
The SO\textsuperscript{3\(\text{-}\)} and HSO\textsuperscript{3\(\text{-}\)} ions in the surface water droplets probably enter the stomatal openings from where they move into guard cells, then across a chain of epidermal cells until they reach a point where passage into the inner cells is possible. Sulphur dioxide and H\textsubscript{2}SO\textsubscript{3} are both capable of converting disulfide enzymes or proteins to thiosulphonate and thiols.

The S-S bonds in polypeptide chains are cleaved by H\textsubscript{2}SO\textsubscript{3} (Bailey and Cole, 1959; Cecil and Wake, 1962). The accumulation of HSO\textsuperscript{3\(\text{-}\)} and SO\textsuperscript{3\(\text{-}\)} ions can disrupt the natural balance between incompletely oxidized sulphur compounds and the sulphhydryl groups present in glutathione and cysteine that are essential for the structural integrity of proteins (McMullen, 1960; Loughman, 1964).

Before the emergence of visible symptoms of tissue damage, productivity may be affected by reduced gross photosynthesis, enhanced respiration and a reallocation of photosynthate (Smith, 1990; Meng, 1994).

(b) Oxides of Nitrogen

The three oxides of nitrogen normally encountered in the atmosphere are nitrous oxide (N\textsubscript{2}O), nitric oxide (NO) and nitrogen dioxide (N\textsubscript{2}O\textsubscript{3}). Oxides of nitrogen are generated normally through fossil fuel combustion, biomass burning, lightening and microbiological emission from both natural and agricultural soil, while NH\textsubscript{3} stems from such sources as volatilization from animal waste and synthetic fertilizers, biomass burning, emissions from human excreta and waste, industrial processes and fossil fuel combustion (Bouwman et al., 1997; Lee et al., 1997).

Colourless and odourless nitric oxide (NO) and pungent red-brown nitrogen dioxide (NO\textsubscript{2}) are very important in polluted air. Collectively designated NO\textsubscript{x}, these
gases enter the atmosphere from natural sources, such as lightening and biological processes and from pollutant sources. The latter are much more significant because of regionally high NO$_2$ concentrations, which can cause severe air quality deterioration.

Nitric oxide is biochemically active and less toxic than NO$_2$. Like carbon monoxide and nitrite, NO attaches to hemoglobin and reduces oxygen transport efficiency. NO$_x$ causes (higher doses) bronchitis and other lung diseases. Nitrogen oxides are known to cause fading of dyes and inks used in some textiles. Much of the damage to materials caused by NO$_x$, such as stress corrosion cracking of electrical apparatus, comes from secondary nitrates and nitric acid. In case of vegetation, higher concentration of NO$_2$ damages the leaves of some plants and retards photosynthesis. Exposure to 10 ppm of NO can cause a reversible decrease in the rate of photosynthesis.

Nitrous oxide (N$_2$O) constitutes only 350 parts per billion (ppb) of the atmosphere, and combustion of fossil fuels is now its major source of production (Muzio & Kramlich, 1988). Nitrification and denitrification in soils produce nitric oxide (NO) which plays a key role in the chemistry of the troposphere. The largest production of NO in the atmosphere most likely results from combustion processes. It is also formed by lightening during thunderstorms. In the stratosphere, nitric oxide is produced by the oxidation of N$_2$O and by dissociative ionization of air with injection into the atmosphere of cosmic particles and solar protons. Because of the small lifetime of NO and NO$_2$ in the atmosphere, the geographic and temporal distributions of these gases are highly variable. At high temperatures, the atmospheric nitrogen can be oxidized to NO$_3$ or NO$_2$. 
Oxides of nitrogen represent important precursors of photochemical oxidants. As wet and dry depositions, they also interfere with the mineral economy and the H⁺ budget of the soil, thus influencing the plant metabolism indirectly. Furthermore, NOₓ also act directly upon the above-ground plant parts (Klumpp et al., 1989).

Penetration of phytotoxic gases into plants occurs mostly through stomata and in a dissolved form. However, the proposed main deposition sites may be the leaf surface and sub-stomatal cavity for highly reactive, water-soluble gaseous HNO₃, the substomatal cavity and spongy mesophyll for SO₂ and the whole intercellular surface for O₃, a gas with low water solubility (Taylor et al., 1988). Surface deposition may be 80% of total deposition for HNO₃ in contrast to about 10% for NO₂, 20% for O₃ and 30% for SO₂.

Although nitrous oxide (N₂O) is relatively inert in the troposphere, it absorbs infrared radiation. It can also photochemically decompose in the stratosphere to produce NO₃ which can react with ozone (Crutzen, 1981). The atmosphere contains about 1.500 Tg (Terra gram = 10¹²g) of N₂O. Perhaps 90% of the emissions are derived from soil through biologically-mediated reactions of nitrification and denitrification. Emission of N₂O may be perceived as a leakage of intermediate products in each of these processes. While soils are a major source of N₂O, they also serve as a sink (Fenney et al., 1978). Generally, the N₂O emissions are proportional to the nitrifiable N content of the soil (Minami and Fukushi, 1983). N₂O is more likely to continue to be reduced to N₂ in the denitrification cycle or to be leached with percolating waters because N₂O is fairly soluble in water.

Nitrogen dioxide (NO₂), an air pollutant, may be absorbed and assimilated by plants to serve as a source of nitrogen. After foliar entry, gaseous pollutant NO₂
reacts with either extracellular water or cell sap to produce equal amounts of nitrate and nitrate ions which are incorporated in the N-metabolism of the cell by the action of nitrite and nitrate reductases (Klumpp et al., 1989).

Plants metabolize the dissolved NO\textsubscript{x} through nitrate assimilation pathway; nitrate is reduced to nitrite. When dissolved in rain water, NO\textsubscript{2} may reach plants in the form of HNO\textsubscript{3} and HNO\textsubscript{2} which may be absorbed either by leaves or by roots if the acids settle down in the soil. The acidic nature of NO\textsubscript{2} affects the electron flow and photophosphorylation in plants. At a given atmospheric concentration, NO may be less toxic than NO\textsubscript{2} due to its slower uptake. The solubilities of both gases (NO and NO\textsubscript{2}) are quite different; NO\textsubscript{2} immediately reacts with water but NO, by contrast, is almost insoluble (2 \( \mu \) moles ml\textsuperscript{-1}). Consequently, uptake rates by plants are twelve fold faster for NO\textsubscript{2} than for NO (Bennett and Hill, 1975). The absorbed NO\textsubscript{2} gas is easily converted to NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2} before further utilization in plant metabolism (Yoneyama and Sasakawa, 1979; Kaji et al., 1980).

Emission of nitrous oxide increases with increased pH, organic matter and temperature (Bremner and Blackmer, 1981; Freney et al., 1979). Addition of P fertilizers and CaCO\textsubscript{3} (pH raised from 5.1 to 6.8) has also been shown to increase N\textsubscript{2}O emission from aerobic soils, presumably by increasing the activity of the nitrifying population (Minami and Fukushi, 1983). Production of N\textsubscript{2}O from nitrification occurs whenever conditions allow nitrification, but emissions are greatly affected by moisture, plant cover, tillage, soil drying and rewetting, freezing and thawing and the amount of nitrate present.

Nitric oxide and nitrous oxide (collectively called NO\textsubscript{x}) are thought to be not as important in absorbing light energy as N\textsubscript{2}O but they are involved in important
atmospheric reactions. When NO is in sufficient concentration (10 ppb), it oxidizes CH₄ and CO and causes the formation ozone (O₃) and hydroxyl radicals. Hydroxyl radicals are the main purifying agents in the troposphere. Lower concentrations of NO may cause a net loss of ozone and hydroxyl radicals. NO₂ can cause destruction of ozone, particularly in the stratosphere (Bouwman, 1989) and NO₂ reacts with hydroxyl ions in a photochemically activated reaction to form nitric acid. Soil and environmental factors that affect nitrification also influence N₂O emission via the nitrification process. There may be at least three factors that are affecting N₂O emissions: 1) Soil pH may be an important factor in controlling production of substrate for N₂O production viz., denitrification and nitrification. Perhaps immobilization of mineral N may be another factor controlling net availability of mineral N for nitrification and subsequent denitrification, 2) Deficiency of nutrients, such as P, may be implicated in N mineralization and nitrification, which affects N₂O emissions, 3) The possibility of some toxic substances being produced in a soil ecosystem, which then affect nitrification and N mineralization, because these inhibitory substances may be important in controlling the population of nitrifiers and denitrifiers involved in N₂O production (Annaduri et al., 1995).

Nitrous oxide is the source of various oxides of N that catalyze the destruction of ozone by photochemical reaction (Crutzen, 1981). These can be represented as follows:

\[ O_3 + hv \rightarrow O + O_2 \]
\[ O + NO_2 \rightarrow NO + O_2 \]
\[ NO + O_3 \rightarrow NO_2 + O_2 \]
This series of reactions results in the net loss of ozone, which can be represented as:

$$2O_3 \rightarrow 3O_2$$

The denitrification has been considered the major source of $N_2O$ in soils and waters (CAST, 1976; Delwiche, 1981), it is now recognized that nitrification may also contribute to $N_2O$ emissions. Nitrous oxide also can be formed by chemical reactions when $NH_2OH$ is decomposed in acid soils producing small amounts of $N_2O$ (Nelson and Bremner, 1970), but these processes contribute relatively little to $N_2O$ production in soils compared to nitrification and denitrification.

Oxides of Carbon

Carbon monoxide (CO) is a colourless, odourless gas. It is a product of an incomplete combustion of carbon-containing compounds.

Most of the CO in the ambient air comes from vehicle exhaust. Internal combustion engines do not burn fuel completely to $CO_2$ and water; some unburned fuel will always be exhausted with CO as a component. CO tends to accumulate in areas of concentrated vehicle traffic, in parking garages, and under building overhangs. Much of this is present as an intermediate in the oxidation of methane by hydroxyl radical.

CO is highly poisonous to human and animals due to having a strong affinity for haemoglobin. It interferes with the haemoglobin's natural function of carrying $O_2$, i.e.

$$Hb + O_2 \rightarrow HbO_2 \text{ or } O_2Hb$$

CO competes with $O_2$ for sites of haemoglobin so as to combine with the latter to form CO Hb. The normal level of COHb in the human blood cell is about 0.5%. It increases with increasing levels of CO in the atmosphere. It also depends on the total
duration of exposure. CO poisoning is reversible except in the worst cases. CO poisoning can be cured by exposing the affected person to fresh air whereby a reverse reaction can occur as:

\[
\text{COHb} + \text{O}_2 \rightarrow \text{O}_2\text{Hb} + \text{CO}
\]

The major sink process for CO is atmospheric oxidation to CO\(_2\), a rather slow process involving free radicals such as OH and H\(_2\)O. Complete oxidation requires a high temperature and a sufficiently long period of time.

When fossil fuels are burnt for producing energy, carbon dioxide and water vapour are emitted into the atmosphere. Emissions of carbon dioxide are significant in as much as it is the major greenhouse gas. CO\(_2\) molecules absorb heart energy and do not allow it to radiate into space. As a result, the earth’s mean temperature increases. This may lead to melting of polar ice caps and flooding of the low-lying lands all over the world.

Plants play a major role in the global carbon balance. Atmospheric CO\(_2\) is important for plants as a substrate for photosynthesis by which CO\(_2\) is fixed and reduced to carbohydrate. Photosynthetic activity of terrestrial and aquatic plants removes carbon from the atmosphere, while plant respiration and decomposition of organic matter release carbon back into the atmosphere. The concentration of atmospheric CO\(_2\) has increased from 280 \(\mu\)l l\(^{-1}\) about 230 years ago to 365 \(\mu\)l l\(^{-1}\) today and a further increase to 700 \(\mu\)l l\(^{-1}\) is foreseen within 100 years (Allen, 1990).

CO\(_2\) levels in the atmosphere cause accelerated uptake of this gas by plants undergoing photosynthesis, which results in a slow buildup of atmospheric CO\(_2\). It is one of the basic requirements for photosynthesis and its excess will increase plant growth and yield. However, extremely high concentrations will have detrimental effects on plants.
At the global scale, the terrestrial higher plant respiration might release in the order of ten times as much carbon to the atmosphere each year as is released by fossil fuel combustion. For these reasons, any effects of elevated atmospheric CO$_2$ on respiration have an important implication for plant growth, ecosystem productivity and the global carbon cycle. For a wide range of plants and climatic conditions the net CO$_2$ exchange initially increased by 52% with doubling the ambient atmospheric CO$_2$ concentration, but plants got acclimated to elevated CO$_2$, and stimulation of photosynthetic rate declined to about 29% (Cure and Acock, 1986). In general, low CO$_2$ concentration enhances stomatal opening, whereas increased CO$_2$ concentration causes closure (Raschke, 1979). The stomatal closure in response to high levels of CO$_2$ tends to increase the ratio of photosynthesis to transpiration, thus increasing the water use efficiency (WUE) on a per unit leaf area basis. This is because the flux of water vapour from the leaf is relatively more sensitive than photosynthesis to changes in stomatal resistance. With other environmental conditions maintained at optimum levels, a doubling of CO$_2$ may lower the transpiration by 25-50% and increase the WUE per unit leaf area as much as twofold (Pearcy and Björkman, 1983; Cure and Acock, 1986). ‘Intercellular’ CO$_2$ concentration within the substomatal cavity of plant leaves (or the internal CO$_2$) depends on (i) ambient CO$_2$ concentration, (ii) the stomatal conductance, which controls the flux of CO$_2$ into the intercellular air space; and (iii) the rate of CO$_2$ assimilation by photosynthetic enzymes, which controls the flux of CO$_2$ from the intercellular air space into mesophyll cells. Thus internal CO$_2$ often increases with increase in ambient CO$_2$ concentration, but the pattern change in the former depends on the rate of photosynthetic activity and the feedback effect associated with the stomatal-closure
response to increase in the intercellular as well as the ambient \( \text{CO}_2 \) concentrations (Wolfe, 1995).

Elevated \( \text{CO}_2 \) levels may reduce stomatal densities, and increase photosynthetic rate, leaf area, plant biomass and overall yield (Allen, 1990; Kimball et al., 1990; Samarakoon et al., 1995; Slafer and Rawson, 1997). However, photosynthetic stimulation to elevated \( \text{CO}_2 \) seems to decline with long-term exposures (Shin, 1990). Typically, stomatal conductance will decrease by 30-40% when plants are exposed to a short-term doubling of \( \text{CO}_2 \) (Morison, 1987; Mott, 1990). Increases in photosynthates and WUE are caused primarily by accelerated rate of photosynthesis rather than reduced transpiration (Allen, 1990).

(d) Ozone

Ozone (\( \text{O}_3 \)) is another widespread phytotoxic air pollutant in the lower troposphere though not so prevalent in our region. Ozone, a highly irritating oxidizing gas, has a diurnal pattern, typically increasing on sunny days with warm temperatures which accelerate the photochemical synthesis reactions, involving oxygen, \( \text{NO}_x \), volatile organic compounds (VOCs) and peroxides. Ozone is not emitted directly into the air, but is the result of chemical reactions in the ambient air. The components of automobile exhaust are particularly important in the formation of atmospheric ozone which is a strong photo-oxidant that may adversely affect the biotic and abiotic components of the environment. Concentrations of a few parts per million can produce pulmonary congestion, edema and pulmonary hemorrhage. Symptoms of ozone and oxidant exposure are a dry throat, followed by headache, disorientation and altered breathing patterns. At sufficient concentrations, ozone produces tissue collapse.
and markings of the upper surface of the leaf known as stipple (pigmented red-brown) and flecking (bleached straw to white).

Ozone enters the plant mainly through its open stomata. The rapidity of changes observed does suggest that ozone penetrates beyond plasmalemma into the cell (Guderian et al., 1985). The plasma membrane has been implicated as the initial site of injury (Doming and Heath, 1985) with inhibition of K\(^+\)-stimulated ATPase of the plasmalemma and changes in cell membrane permeability leading to osmotic or ionic imbalance within the cell, but this is unlikely to be the only effect (Dugger and Tinz, 1970; Evans and Ting, 1973; Mudd et al., 1984).

Plant responses to ozone are influenced by ambient radiant energy in terms of intensity, quality and duration. The light intensity under which a plant has been grown may be expected to affect plant sensitivity to ozone (Darrall, 1989). At the time of exposure, plants may be most sensitive at both low and high intensities of light and least sensitive at intermediate level (Carlson, 1979).

Ozone oxidizes plant surfaces and tissues and affects many important physiological processes (Darrell, 1989). It is particularly injurious to membranes and notably inhibits photosynthesis and biomass accumulation, suppresses phloem loading, and reduces carbon allocation to the roots. The symptoms of visible injury take many forms and usually include changes in the pigmentation. The symptoms vary with species and may include chlorotic or necrotic spotting, flecking or blotching and browning or reddening. Chlorosis may appear as an upper leaf surface stipple and necrosis may be bifacial. Ozone stress has been shown to reduce total plant dry weight, leaf area; leaf area duration; relative growth rate of leaves, stems and roots, and the net assimilation rates (Endress and Grunwald, 1985; Krupa and Kickert, 1989).
Suspended particulate matter (SPM)

Small, solid particle and liquid droplets are collectively called particulates. These are present in the atmosphere in fairly large numbers and often pose a serious air pollution problem. Suspended particulate matter is a complex with respect to particle size distribution, the chemical composition and its sources (Monn, 2001). Particulate air pollutants are very diverse in character including both organic and inorganic substances with diameters ranging from < 0.01-100 μm. Fine particles present the highest sulphur contents (almost 100%), while calcium is the major element in the medium and coarse particles. Other abundant elements are silicon, chlorine and phosphorus. The amount of sulphur-rich particles decreases as particle size increases, but the presence of sulphur increases in the very coarse fraction due to the deposit of big flyash (Esbert et al., 2001).

Particulates include organic matter, nitrogen compounds, sulphur compounds, several metals, smaller ash particles and radionuclides, and occur in the form of dust (solid particles, range from 0.1 micron to 10 mm in diameter), mist (liquid particles, range from 0.5 to 3.0 μm in diameter), fume (solid particles, range from 0.03 to 0.3 μm in diameter), and/ or smoke (solid particles, 0.05 to 1 μm in diameter).

Coal combustion in power stations gives rise to emission of primary (direct emissions) and secondary (gas to particle conversion) particulate pollutants. While the emission of pollutants depends on coal quality and combustion technology, the transport, transformation and deposition of contaminants depend on regional climatic conditions (Querol et al., 1998).

Virtually every industrial process is a potential source of dust, smoke or aerosol emissions, including waste incineration, coal combustion, combustion of heavy oil and smelting.
Particulate carbon as soot, carbon black, coke and graphite originates from auto and truck exhausts, heating furnaces, incinerators, power plants and steel and foundry operation and composes one of the more visible and troublesome particulate air pollutants. Because of its good absorbent properties, carbon can be a carrier of gaseous and other particulate pollutants. The combustion of fossil fuels containing high ash content results in the smaller ash particles called 'fly ash' which emerge from the stack and enter the atmosphere. The composition of fly ash varies widely, depending upon the source of fuel. The predominant constituents are oxides of aluminum, calcium, iron and silicon. Other elements that occur in fly ash are magnesium, sulphur, titanium, phosphorus, potassium and sodium. Elemental carbon (soot, carbon black) is a significant fly ash constituent.

Particulate controls in power station have a high efficiency rate (nearly 99.9% for electrostatic precipitators), but considerable amounts of flyash are discharged into the environment due to high coal consumption. A 1000 MW power station with a normal consumption of 12,000 t of sub-bituminous coal d\(^{-1}\) has a mean combustion waste production of about 2,400 d\(^{-1}\). If the 99.9% efficiency rate is assumed for the electrostatic precipitators, almost 900 tonnes of flyash per year are transferred to the atmosphere as primary particulate pollutants. These primary alumino-silicate particles may reach > 20 \(\mu\)m in diameter (Querol, et al., 1996). Once emitted into the atmosphere, primary flyash particles and secondary aerosols are carried and dispersed by atmospheric motions over a wide range of scales, and deposited on the ground at distances ranging from several to hundreds of kilometers from the emission point.

In addition to the primary flyash emissions, the gas-to-particle conversion processes also give rise to considerable volumes of highly reactive secondary particulate pollutants after oxidation of sulphur and nitrogen oxides.
The residence times for SO$_2$ in the lower troposphere have been shown to vary from $< 1$ to $4$ d (Gillani and Wilson 1980; Gillani et al., 1981; Manson 1992; Hidy 1994). Given this, the power plants with high SO$_2$ and/or NO$_x$ emission, must have emission of secondary particulates in much higher a magnitude than that of primary particulates. Grain size of secondary particles lies around $0.2 - 1.0 \mu m$ for sulphate and $2.5$ to $5.0 \mu m$ for nitrates (Pakanen, 1996; Querol et al., 1998) which is very fine in comparison with primary-flyash particles. The natural atmospheric particulate input exerts a great influence not only over the bulk particulate levels but also over the neutralization of acidic wet and dry deposition of secondary species (Avila and Roda, 1991; Caboi et al., 1992; Avila, 1996; Carratala et al., 1996; Quereda et al., 1996).

The air-borne particulate matter has been shown to have adverse effects on human health and environment (QUARG, 1996). The most obvious of these, is reduction and distortion of visibility. Particles smaller than about $0.1 \mu m$ in diameter, have an insignificant effect upon visibility in the atmosphere. Small particles can enter the body through a number of ways. They can cause eye irritation. Respiratory system may be damaged directly by particulate matter that enters the blood system or lymph system through the lungs.

Particulate matter can have severe effects on vegetation. When thick enough, soot coatings can prevent photosynthesis and block the stomata of leaves. Fly ash, under certain condition of humidity, sticks to the leaves or fruits and promotes chemical as well as physical injuries. Fly ash particles, concentrated on the surface of the guard cells, affect the mechanism that regulates the opening and closing of the stomata and often prevents their closing by blocking the stomatal aperture (Fluckiger...
et al., 1979; Krajchava and Majstrick, 1984), thereby allowing increased transpiration (Mishra and Shukla, 1986). Thick layer of flyash also interferes with light required for photosynthesis and thus reduces the photosynthetic rate. Leaves laden with flyash, absorb radiation more effectively. Consequently, the temperature of the dusted leaves rises resulting in increased transpiration.